Tetrahedron, 1958, Vol. 2, pp. 203–210. Pergamon Press Ltd., London

SYNTHESIS OF BENZO-FURAN DERIVATIVES—I

KARANJ KETONE, KARANJIN AND PONGAPIN

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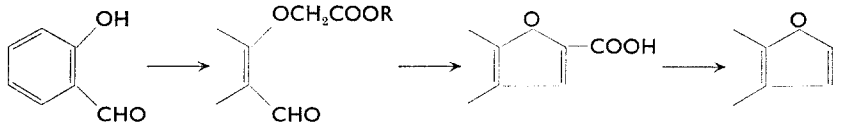
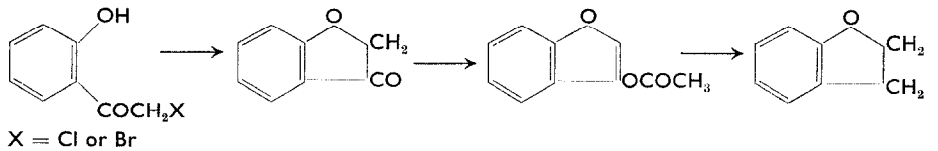
Abstract—A new method of preparing benzo-furan derivatives using substituted allyl phenols has been worked out. Ozonolysis of the allyl derivatives and subsequent ring closure of the resulting *o*-hydroxy-acetaldehydes by means of *o*-phosphoric acid give good yields of karanj ketone, karanjin, pongapin and the corresponding 2-methyl furanochromone. As an alternative route oxidation of the allyl phenol in two stages using performic acid followed by periodic acid has been successfully employed in the synthesis of karanjin.

Two general methods have been extensively used in the past, for constructing a furan ring on a benzene ring, in connexion with the syntheses of naturally occurring benzo-furan derivatives and especially the furano benzo-pyrones. The first starts from an *o*-hydroxy aldehyde and follows the steps shown below:[1]



The main difficulty in this method seems to be the lack of availability of the required *o*-hydroxy aldehyde system particularly when the furan unit has to be built up on an already available pyrone system. Frequently it is also difficult to prepare the carbethoxy methyl ether of a hydroxyl group which is *o*-*o*′-disubstituted. Another very serious difficulty which has been experienced in adopting the method for the synthesis of angular furanopyrones[2] (e.g. karanjin) is the decarboxylation of the intermediate furan-5′-carboxylic acid at the last stage. Though successful recently,[3(a),3(b)] it gives extremely poor yields. The second method consists in the cyclisation of an *o*-hydroxy-*ω*-halo acetophenone and converting the resulting coumaran-3-one into a coumaran by the reduction of the enol acetate as shown below:[4]

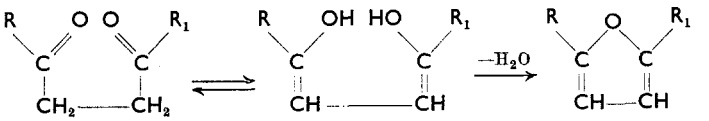


The coumaran thus obtained has to be dehydrogenated to the furan at the last stage and this frequently leads to very poor yields.

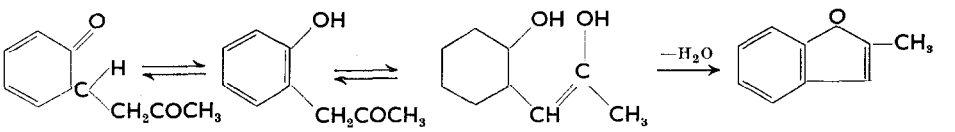
[1] A. Rössing *Ber. Dtsch. Chem. Ges.* **17**, 2988 (1884); R. C. Elderfield *Heterocyclic Compounds* Vol. II, p. 14. Wiley, New York (1951).
[2] S. Rangaswami and T. R. Seshadri *Proc. Ind. Acad. Sci.* A **9**, 259 (1939).
[3(a)] L. R. Row and T. R. Seshadri *Proc. Ind. Acad. Sci.* A **33**, 168 (1951).
[3(b)] L. R. Row and T. R. Seshadri *Proc. Ind. Acad. Sci.* A **34**, 187 (1951).
[4] R. L. Shriner and J. Anderson *J. Amer. Chem. Soc.* **60**, 1418 (1938).

Since the benzo-furan system is present in a large number of naturally occurring compounds, many of them having important drug activity, attempts have been made in this laboratory to develop newer methods of building up the furan ring starting from more easily available intermediates. One such successful method is reported in this paper.

Ring closure involving *cyclo*-dehydration of 1:4-dicarbonyl compounds represents one of the oldest and most convenient methods for the preparation of furan derivatives.[5]

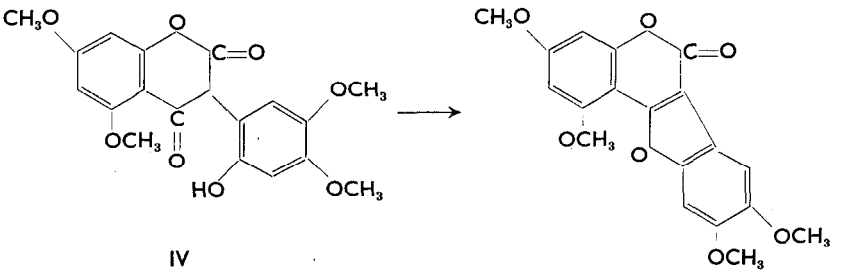


The method is capable of wide application and appears to be limited only by the availability of the requisite dicarbonyl compounds. An *o*-hydroxy phenyl acetone (II) is in effect the mono-enolic form of the 1:4-dicarbonyl compound (I) and yields benzofuran derivative (III) on *cyclo*dehydration.



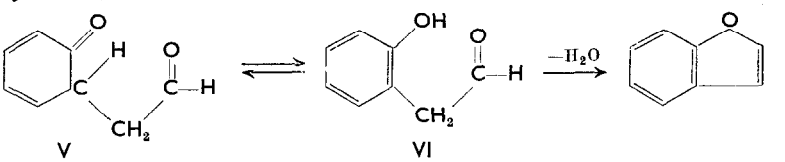
I II III

Preparation of 2-methyl-5-nitro coumarone from 2-hydroxy-5-nitro phenyl acetone is the earliest known example of such a synthesis.[6] More recently similar intermediates (IV) have been employed for the syntheses of compounds containing fused benzo-furan nucleii.[7]



IV

For the synthesis of a simple unsubstituted benzo-furan system the required 1:4-dicarbonyl derivative would be (V) of which the mono-enol form is *o*-hydroxy phenyl acetaldehyde (VI).

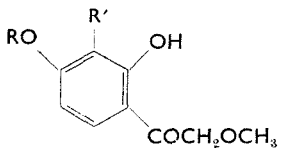


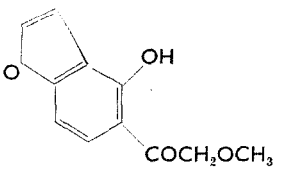
V VI

[5] C. Paal *Ber. Dtsch. Chem. Ges.* **17**, 2765 (1884).
[6] W. J. Hale *Ber. Dtsch. Chem. Ges.* **45**, 1596 (1912).
[7] T. R. Govindachari, K. Nagarajan and P. C. Parthasarathy *J. Chem. Soc.* 548 (1957); W. J. Bowyer, A. Robertson and W. B. Whalley *J. Chem. Soc.* 542 (1957).
See also J. N. Chatterjea *Experientia* XII/10, 371 (1956); J. N. Chatterjea and S. K. Roy *J. Ind. Chem. Soc.* **34**, 98 (1957).

The *o*-hydroxy phenyl acetaldehyde derivatives required for the present work have been prepared from the corresponding *o*-hydroxy allyl compounds by two well-known methods. The first and the better one is the ozonolysis of the allyl compound. Alternatively the allyl double bond is hydroxylated by performic acid and the resulting *vic*-glycol cleaved by periodic acid. Cyclisation of these intermediate acetaldehydes have been most successfully accomplished by means of hot *o*-phosphoric acid which also served as suitable solvent for the reaction.

The first case, where this method was quite successful, was the synthesis of a benzofuran derivative, karanj ketone (X). This is a fission product of karanjin (XIV) and was earlier synthesised from γ-resorcylic aldehyde (itself difficult to prepare) involving about eight steps giving low yields.[8] In the present method the required allyl intermediate was 2:4-dihydroxy-3-allyl-ω-methoxy acetophenone (VIII) which was most conveniently prepared by the Claisen migration of the partial allyl ether of ω-methoxy resacetophenone (VII). The constitution of the product is based on analogy with the related resacetophenone derivative studied earlier by Baker and Lothian.[9] Ozonolysis of the allyl derivative (VIII) proceeded very satisfactorily in ethyl acetate solution, excess of ozone being employed. Catalytic hydrogenation of the ozonide in the same solvent yielded ω-methoxy resacetophenone-3-acetaldehyde (IX) in excellent yield. Cyclisation of it by *o*-phosphoric acid gave a quantitative yield of karanj ketone (X).





VII R = $-CH_2-CH=CH_2$; R′ = H
VIII R = H; R′ = $-CH_2-CH=CH_2$
IX R = H; R′ = $-CH_2-CHO$

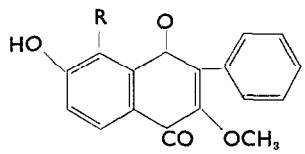
X

In order to test the suitability of this method for building up a furan ring on a flavone unit the synthesis of karanjin (XIV) was next attempted. Karanjin, which occurs in *Pongamia glabra*, is one of the earliest known furano-flavones. Its constitution was established by Limaye[10(a)] and by Manjunath *et al.*[10(b)] and later it was synthesised by Seshadri *et al.*[3(a)] from 3-methoxy-7-hydroxy flavone-8-aldehyde (XI) in poor yields. After a number of trials in the course of the present work the most suitable solvent for ozonolysis of the required intermediate 3-methoxy-7-hydroxy-8-allyl flavone (XII) was found to be formic acid. The main difficulty in this case was the low solubility of the hydroxy allyl compound in the usual solvents employed for ozonolysis. Excess of ozone in this case had to be avoided since the pyrone double-bond is also susceptible and it was found always safer to leave the reaction incomplete and remove the unchanged allyl compound (reduced, in the subsequent step, to the corresponding propyl compound) at a later stage. The intermediate acetaldehyde (XIII) could not, therefore, be obtained pure and was characterised by forming a derivative. It was directly used for cyclisation in the next step giving a good yield of

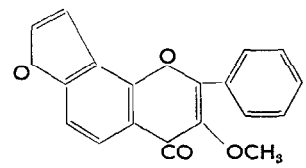
[8] T. R. Seshadri and V. Venkateswarlu *Proc. Ind. Acad. Sci.* A **13**, 404 (1941).
[9] W. Baker and (Miss) O. M. Lothian *J. Chem. Soc.* 628 (1935).
[10(a)] D. B. Limaye *Abs. Ind. Sci. Congress* 151 (1926).
[10(b)] B. L. Manjunath, A. Seetharamiah and S. Siddapa *Ber. Dtsch. Chem. Ges.* **72**, 93 (1939).

karanjin (XIV). Experiments using the more soluble acetate of the allyl flavone led to the fission of the pyrone ring during ozonolysis, the only isolable product being benzoic acid.

Because of the limitations of the ozonolysis in this case, the second route was also explored. Oxidation of the acetate of the hydroxy allyl flavone (XII) using performic acid and subsequent alkaline hydrolysis of the formic ester gave a fair (60 per cent) yield of the corresponding 1:2 diol (XV). Oxidative degradation of the diol (XV) in alcoholic solution with periodic acid gave the required acetaldehyde (XIII) which could not be crystallised but was directly cyclised to karanjin. Yields in this oxidation, however, were not good and on the whole the first method was preferable.

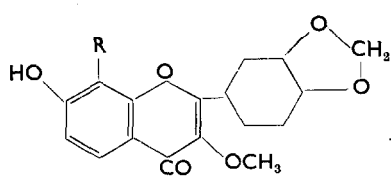


XI R = —CHO
XII R = —CH_2—CH=CH_2
XIII R = —CH_2—CHO
XV R = —CH_2—CHOH—CH_2OH

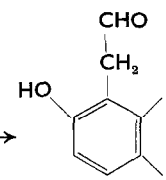


XIV

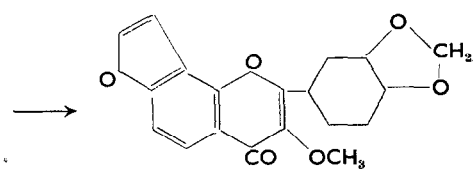
As a more complex naturally occurring furano-flavone, pongapin (XVIII) has also been synthesised. It occurs in the Australian plant *Pongamia pinnata* L. Merr and was earlier synthesised from karanj ketone.[11] For the present synthesis 3-methoxy-7-hydroxy-3′:4′-methylenedioxy-8-allyl flavone (XVIa) was ozonised in formic acid solution and the resulting aldehyde (XVII), on cyclisation, yielded pongapin (XVIII). The extremely poor solubility of the hydroxy allyl flavone even in formic acid caused some difficulty and success could be achieved by working with dilute solutions. Here also use of excess of ozone or a soluble derivative like the acetate caused oxidation of the pyrone double bond yielding piperonylic acid. Attempts to use the second route in this case were not successful.



XVI
(a) R = —CH_2—CH=CH_2
(b) R = —CH_2—CHOH—CH_2OH



XVII

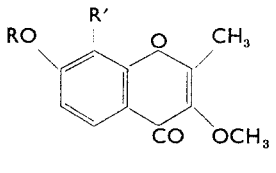


XVIII

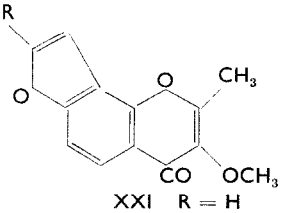
The synthesis of the related simple 2-methyl furano-chromone (XXI) was next done following the same general procedure. This chromone (XXI) is not naturally

[11] L. R. Row *Aust. J. Sci. Res.* A 5, 754 (1952).

occurring but it was synthesised earlier by the Kostanecki acetylation of karanj ketone by Manjunath *et al.*[12] Ozonolysis of the *o*-hydroxy allyl chromone (XIX) in formic acid and cyclisation of the resulting 8-acetaldehyde (XX) (characterised as the 2:4-dinitrophenyl hydrazone) yielded the furano-chromone (XXI). An attempt was made to prepare an authentic sample of it starting from the readily available 2-methyl-3-methoxy-7-hydroxy chromone-8-aldehyde (XXII) and following the bromacetic ester method. The hydroxy aldehyde (XXII) gave the corresponding carbethoxy methyl ether (XXIII) when heated with bromacetic ester and potassium bicarbonate in acetone solution. Use of potassium carbonate led to the formation of a potassium salt which remained unchanged even after long boiling. The strong acid nature of the 7-hydroxyl group in the compound is worth mentioning; the substance is soluble in sodium bicarbonate just like carboxylic acids.[13] The carbethoxy methyl ether (XXIII) was cyclised to the furan-5′-carboxylic acid (XXIV) by means of sodium ethoxide in alcoholic solution. Decarboxylation of it using both quinoline-copper powder and sodium acetate-acetic anhydride methods, however, yielded only resinous substances from which no pure product could be isolated. The required authentic sample of the chromone (XXI) was, therefore, made from karanj ketone.



XIX R = H; R′ = —CH_2—CH=CH_2
XX R = H; R′ = —CH_2—CHO
XXII R = H; R′ = —CHO
XXIII R = —CH_2·COO Et; R′ = —CHO



XXI R = H
XXIV R = —COOH

EXPERIMENTAL

2-Hydroxy-4-allyloxy-ω-methoxy acetophenone (VII). A solution of ω-methoxy resacetophenone (5·8 g) in dry acetone (150 cc), containing allyl bromide (2·8 cc), was refluxed with potassium carbonate (10 g) for 5 hr. Evaporation of the filtered solution and fractionation of the residual brownish oily liquid gave the following; (a) recovered material (1·0 g) obtained as the sodium carbonate soluble fraction, (b) 2-hydroxy-4-allyloxy-ω-methoxy acetophenone (3 g), a pale yellow viscous liquid, obtained as the sodium hydroxide soluble fraction (2:4-dinitrophenyl hydrazone, crimson plates from alcohol, m.p. 174–5°C. Found: C, 53·9; H, 4·8: Calc. for $C_{18}H_{18}O_7N_4$: C, 53·7; H, 4·5%), (c) 2:4-diallyloxy-ω-methoxy acetophenone (0·5 g), a colourless oily liquid, as the sodium hydroxide insoluble fraction (2:4-dinitrophenyl hydrazone, orange plates from alcohol, m.p. 132–3°C. Found: C, 57·0; H, 5·0. Calc. for $C_{21}H_{22}O_7N_4$: C, 57·0; H, 5·0%).

Refluxing the mixture for a longer time did not improve the yield of the partial allyl ether, more of the diallyl ether being formed.

2:4-Dihydroxy-3-allyl-ω-methoxy acetophenone (VIII). The partial allyl ether (3 g) underwent smooth Claisen migration when kept for 2 hr at 190–95° under reduced pressure. The migrated product (2 g) was isolated as the sodium carbonate soluble fraction. It crystallised from dilute alcohol as colourless long needless melting at

[12] B. L. Manjunath and A. Seetharamiah *Ber. Dtsch. Chem. Ges.* **72**, 97 (1939).
[13] See also K. Aghoramurthy and T. R. Seshadri *J. Chem. Soc.* 3065 (1954).

139–39·5° (Found; in a sample dried at 100° in vacuum: C, 64·9; H, 6·1; Calc. for $C_{12}H_{14}O_4$: C, 64·9; H, 6·3%).

2:4-*Dihydroxy-ω-methoxy acetophenone-3-acetaldehyde* (IX). A stream of ozonised oxygen (2%; 150 cc/min) was passed through a cooled (−15°C) solution of the above allyl ketone (0·5 g) in dry ethyl acetate (100 cc) till excess of ozone could be detected in the outlet (approx. 30 min). The ozonide was decomposed by shaking the solution with hydrogen in the presence of palladium–charcoal (5%; 1 g) till one mole of the gas was absorbed. The filtered solution on evaporation yielded the acetaldehydo–ketone (0·3 g). It crystallised from a mixture of ethyl acetate and petroleum ether as colourless stout needles, m.p. 133–133·5° (Found: C, 59·3; H, 5·2 Calc. for $C_{11}H_{12}O_5$: C, 58·9; H, 5·4%). Its aqueous solution reduced Tollens' reagent in the cold and its dimedone derivative crystallised from dilute alcohol as colourless plates, m.p. 182–3°.

Cyclisation of (IX) to *4-hydroxy-5-ω-methoxyacetyl coumarone* (X). A solution of the aldehydo–ketone (0·15 g) in *o*-phosphoric acid (2 cc) was heated in a boiling water bath for 10 min and then poured over crushed ice when a colourless solid separated out. This was extracted with benzene (200 cc), the benzene solution partially concentrated and the concentrate percolated through a short column of activated alumina. The column was washed with fresh benzene (500 cc). The percolate and the washings were mixed together and evaporated to dryness; the residual colourless solid (0·1 g) crystallised from dilute alcohol as rectangular plates, m.p. 96–97° alone or when mixed with an authentic sample of karanj ketone prepared from karanjin. Its acetate, prepared by boiling with acetic anhydride and pyridine, came out of alcohol as colourless hexagonal plates, m.p. 99–100° alone or when mixed with an authentic sample.

3-*Methoxy-7-hydroxy flavone-8-acetaldehyde* (XIII). A stream of ozonised oxygen (4%; 150 cc/min) was passed through a solution of 3-methoxy-7-hydroxy-8-allyl flavone[14] (XII) (0·5 g) in formic acid (50 cc) at 10° for 20 min (the optimum time being found after a number of experiments). The solution was allowed to warm up to room temperature and then shaken with hydrogen in the presence of palladium–charcoal (5%; 0·5 g) until the absorption of hydrogen (approximately 1 mol) ceased. The filtered solution was diluted with ice-water and extracted with chloroform; the extract was washed with ice cold aqueous sodium bicarbonate solution. Evaporation of the solvent yielded the aldehyde as a pale yellow viscous mass which could not be crystallised. It gave a 2:4-dinitrophenyl hydrazone derivative which crystallised from chloroform–alcohol as yellow thin needles, m.p. 220–21° (Found: C, 58·8; H, 3·9. Calc. for $C_{24}H_{18}O_8N_4$: C, 58·8; H, 3·7%).

Cyclisation of (XIII) *to karanjin* (XIV). A solution of the above aldehyde (from 0·5 g. of the allyl flavone) in *o*-phosphoric acid (10 cc) was kept stirred at 120° for 15 min, then cooled and poured on crushed ice. The colourless solid that separated was dissolved in chloroform and the solution chromatographed on a column of activated alumina (50 g). Elution of the column with benzene and evaporation of the solvent yielded karanjin (0·2 g), colourless needles from methanol, m.p. 157–8° alone or when mixed with a sample obtained from *Pongamia glabra*.[15]

[14] B. Krishnaswamy and T. R. Seshadri *Proc. Ind. Acad. Sci.* A **13**, 43 (1941).
[15] D. B. Limaye *Abs. Ind. Sci. Congress* 118 (1925); N.V.S. Rao, J. V. Rao and T. R. Seshadri *Proc. Ind. Acad. Sci.* A **10**, 65 (1939).

Further elution of the alumina column with alcohol gave 3-methoxy-7-hydroxy-8-propyl flavone (0·15 g) as colourless long needles, m.p. 235–6°. Mixed melting point with a sample obtained from 3-methoxy-7-hydroxy-8 allyl flavone (XII) by catalytic reduction was undepressed (Found: C, 73·9; H, 5·9. Calc. for $C_{19}H_{18}O_4$: C, 73·5; H, 5·8%). Its acetate crystallised from alcohol as colourless hairy needles, m.p. 110–11°.

3-*Methoxy*-7-*hydroxy*-8-(*β*:*γ*-*dihydroxypropyl*) *flavone* (XV). A solution of 3-methoxy-7-acetoxy-8-allyl flavone (0·5 g) in anhydrous formic acid (5 cc) was treated with hydrogen peroxide (2 cc; 30%, excess) and the mixture maintained at 40°C for 2 hr. It was then diluted with water (200 cc) and extracted with chloroform (200 cc). The extract was washed with ice cold sodium bicarbonate solution, dried and evaporated. The residual glassy solid could not be crystallised and was, therefore, hydrolysed by keeping a solution of it in aqueous methanolic sodium hydroxide (5%; 5 cc) for 15 min at room temperature. Acidification with dilute hydrochloric acid yielded the diol (0·3 g). It crystallised from dilute alcohol as colourless aggregates of small prisms, m.p. 208–10° (Found: C, 66·6; H, 5·4. Calc. for $C_{19}H_{18}O_6$: requires C, 66·7; H, 5·3%).

Periodic acid oxidation of the diol (XV). The diol (0·1 g) was dissolved in alcohol (35 cc) and treated with periodic acid solution (5 cc; 1·6%). After 6 hr at room temperature with occasional stirring, the mixture was diluted with water (100 cc) and extracted with chloroform. The extract was washed with a solution of sodium sulphite, dried and evaporated. The residual viscous oily material could not be crystallised but gave positive aldehyde test. It was directly cyclised and the product purified in the previous manner yielding karanjin (65 mg) identical with the sample described earlier.

3-*Methoxy*-3′:4′-*methylenedioxy*-7-*hydroxy flavone*-8-*acetaldehyde* (XVII). Ozonolysis of 3-methoxy-3′:4′-methylenedioxy-7-hydroxy-8-allyl flavone[16] (XVI,a) (0·25 g) in anhydrous formic acid (120 cc) at 10°C for 0·5 hr and working up as described earlier yielded the aldehyde as a viscous liquid. It was characterised as the 2:4-dinitrophenyl hydrazone which crystallised as orange prisms form alcohol, m.p. 225–6° (Found: C, 55·9; H, 3·8. Calc. for $C_{25}H_{18}O_{10}N_4$: C, 56·2; H, 3·4%).

Cyclisation of (XVII) *to pongapin* (XVIII). Cyclisation of the crude aldehyde (from 0·25 g allyl flavone) by means of *o*-phosphoric acid as previously described, gave a mixture. Separation of it by chromatography over alumina (10 g) yielded (a) pongapin (50 mg) in the benzene eluent as pale yellow needles from alcohol, m.p. 190–91° alone or when mixed with an authentic sample and (b) 3-methoxy-3′:4′-methylenedioxy-7-hydroxy-8-propyl flavone (40 mg) in the alcohol eluent, as colourless rods from alcohol, m.p. 275–6°. Mixed m.p. of (b) with an authentic sample of the same propyl flavone obtained by the catalytic hydrogenation of the allyl flavone (XVI,a) was undepressed (Found: C, 67·4; H, 5·4. Calc. for $C_{20}H_{18}O_6$: C, 67·8; H, 5·1%).

3-*Methoxy*-3′:4′-*methylenedioxy*-7-*hydroxy*-8-(*β*:*γ*-*dihydroxypropyl*) *flavone* (XVI,b). A solution of 3-methoxy-3′:4′-methylenedioxy-7-acetoxy-8-allyl flavone (0·5 g) in formic acid (15 cc) was treated dropwise with hydrogen peroxide (20 cc; 30%). The mixture was kept at 40°C for 2 hr and then diluted with water. Extraction of the clear aqueous solution with chloroform, washing the extract with aqueous sodium

[16] S. S. Chibber, A. K. Ganguli, S. K. Mukerjee and T. R. Seshadri *Proc. Ind. Acad. Sci.* **47**, 19 (1957).

bicarbonate and evaporation yielded a glassy solid. This was dissolved in methanol (10 cc), the solution treated with aqueous potassium hydroxide (20 cc; 10%) and the mixture kept warm (60°) for 15 min. Acidification with dilute hydrochloric acid yielded the diol (0·4 g). It crystallised from alcohol as pale yellow rods m.p. 225–6° (Found: C, 62·5; H, 4·8. Calc. for $C_{20}H_{18}O_8$: C, 62·2; H, 4·7%).

2-*Methyl*-3-*methoxy*-7-*hydroxy chromone*-8-*acetaldehyde* (XX). Ozonisation of a cooled solution of 2-methyl-3-methoxy-7-hydroxy-8-allyl chromone[17] (XIX) (0·5 g) in formic acid (100 cc) for 0·5 hr and subsequent catalytic hydrogenation of the ozonide yielded the aldehyde as a viscous yellow liquid. Its 2:4-dinitrophenyl hydrazone came out of alcohol as clusters of orange plates, m.p. 249–50° (Found: C, 52·8; H, 3·7. Calc. for $C_{19}H_{16}O_8N_4$:C, 53·3; H, 3·7%).

2-*Methyl*-3-*methoxy furano*-(2′:3′-7:8)-*chromone* (XXI). Heating the crude aldehyde (from 0·5 g of the allyl chromone) with *o*-phosphoric acid (10 cc) at 100° for 15 min and separating the resulting mixture in the usual manner yielded (a) the furanochromone (0·2 g) as colourless rectangular plates from methanol, m.p. 153–4° alone or when mixed with an authentic sample, (b) 2-methyl-3-methoxy-7-hydroxy-8-propyl chromone (0·1 g) as colourless long needles from alcohol, m.p. and mixed m.p. with a sample, prepared from the allyl chromone by catalytic reduction, 216–18° (Found: C, 67·8; H, 6·7. Calc. for $C_{14}H_{16}O_4$: C, 67·7; H, 6·5%). Its acetate, obtained from ethyl acetate as colourless stout rhombs, melted at 103–4°C.

2-*Methyl*-3-*methoxy*-7-*carbethoxymethoxy chromone*-8-*aldehyde* (XXIII). This was prepared earlier by Rangaswami and Seshadri[2] but the following modified method gives better yields. A solution of 2-methyl-3-methoxy-7-hydroxy chromone-8-aldehyde[18] (XXII) (1·0 g) in acetone (75 cc) containing excess of ethyl bromoacetate (2·5 cc) was refluxed with dry potassium bicarbonate (6 g) for 10 hr. It was then filtered, concentrated and cooled. The solid (0·9 g) that separated was filtered and washed with petroleum ether till free from bromacetic ester. On recrystallisation from alcohol, it was obtained as pale yellow plates, m.p. 176–7° alone or when mixed with a sample described by earlier workers.

2-*Methyl*-3-*methoxy*-5′-*carboxy furano*-(2′:3′-7:8)-*chromone* (XXIV). A mixture of the above carbethoxy methyl ether (1 g) and sodium ethoxide from (0·1 g of sodium) in absolute alcohol (100 cc) was shaken vigorously for about 30 min at room temperature during which time the colour of the suspension changed to deep yellow. Cooling and treating the mixture with dry ether precipitated the sodium salts which were then dissolved in water and acidified when the furan 5′-carboxylic acid (0·5 g) separated as a yellow solid. It came from alcohol as small yellow prisms, m.p. 309–11° (d.) (Found: C, 57·5; H, 4·3. Calc. for $C_{14}H_{10}O_6$: C, 57·5; H, 4·1%).

[17] S. Rangaswami and T. R. Seshadri *Proc. Ind. Acad. Sci.* **9**, 4 (1937).
[18] S. Rangaswami and T. R. Seshadri *Proc. Ind. Acad. Sci.* **9**, 7 (1939).