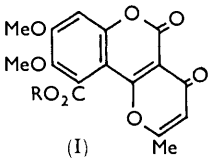
170. *Derivatives of Hydroxyquinol. Part II.*[1] *The Synthesis of 2-Acetyl-4,5,7-trimethoxyindane-1,3-dione: Revised Structures for Some Degradation Products from Citromycetin.*

By F. M. Dean, D. R. Randell, and Graham Winfield.

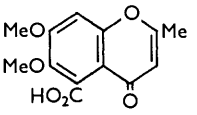
By synthesis of its methyl ether, the degradation product $C_{13}H_{12}O_6$, m. p. 156°, common to both methyl di-*O*-methylanhydrofulvate and methyl di-*O*-methylcitromycetinone, is shown to be 2-acetyl-7-hydroxy-4,5-dimethoxyindane-1,3-dione. The chief step in this synthesis is an ozonolysis of 3,4,6-trimethoxy-2-propenylacetophenone effected by a novel technique.

The course of alkali-degradation of citromycetinone derivatives is elucidated, and revised structures are offered for several of the products.

When citromycetin is converted into methyl di-*O*-methylcitromycetinone (I; R = Me) and hydrolysed by aqueous alkali, an acidic substance $C_{11}H_6O_4(OMe)_2$ is formed that was originally allocated[2] structure (II), this being considered to arise by cyclisation of an intermediate (III). From similar hydrolyses Hetherington and Raistrick[3] obtained also another substance $C_{10}H_6O_3(OMe)_3$ which they thought to be a pyrone, possibly (IV): unable to reproduce this result, subsequent workers[4] proved that 3-hydroxy-6,7-dimethoxy-2-methylchromone (IV), obtained synthetically, had properties widely different from those described in the earlier report. Later workers[5] found sodium methoxide to convert methyl di-*O*-methylanhydrofulvate (V) into the acidic substance thought to be (II), but the further examinations made possible by this discovery led to the suggestion that for this compound structure (VI; R = H) was to be preferred to structure (II). This revision is now confirmed by a synthesis of 2-acetyl-4,5,7-trimethoxyindane-1,3-dione identical with the methyl ether of the degradation product.



(I)



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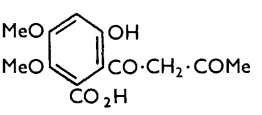

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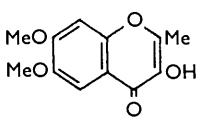

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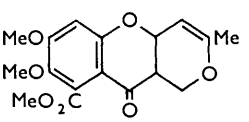

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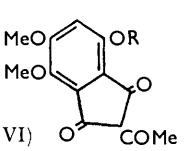


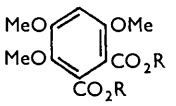
(VI)

Methylation of the degradation product (VI; R = H) gave the ether (VI; R = Me) in accordance with the relative resistance of 2-acetylindane-1,3-dione itself to alkylation. Permanganate oxidation then gave the phthalic acid (VII; R = H), thereby excluding structure (II) but not necessarily proving the correctness of the alternative (VI; R = H).

Though in the past 2-acetylindane-1,3-diones have been made by base-catalysed condensation of alkyl phthalates with acetone, this reaction failed when applied to the phthalate (VII; R = Me). During the exploration of an alternative route it was shown[1] that ozone converts the propenylacetophenone (VIII) into an iso-ozonide so stable that the desired aldehyde could not be obtained from it. Since the last step in the formation of an iso-ozonide is often held to be cyclisation of an intermediate of type (IX), this ozonolysis

[1] Part I, Dean, Randell, and Winfield, *J.*, 1959, 1071.
[2] Robertson, Whalley, and Yates, *J.*, 1951, 2013.
[3] Hetherington and Raistrick, *Phil. Trans.*, 1931, *B*, **220**, 209.
[4] Jones, Mackenzie, Robertson, and Whalley, *J.*, 1949, 562.
[5] Dean, Eade, Moubasher, and Robertson, *J.*, 1957, 3497.

has been re-investigated with the aid of damp ozone so that the water present could compete for the carbonium centre in (IX), promoting fission in the desired direction. This technique gave the aldehyde (X) in good yield along with a little of the stable iso-ozonide. The structure of the aldehyde (X) was confirmed by (*a*) converting it by an internal Cannizzaro reaction into the phthalide (XI), and (*b*) subjecting it to Dakin oxidation. The latter removed the acetyl group selectively, leaving the salicylaldehyde (XII) which condensed with ethyl acetoacetate, giving the coumarin (XIII). Acyl derivatives of 1,2,4,5-tetrahydroxybenzene are not easily accessible, and as formyl derivatives appear not to have been obtained before, this preparation is of general interest.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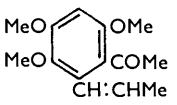
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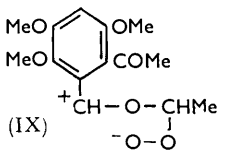
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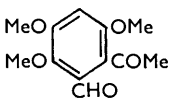
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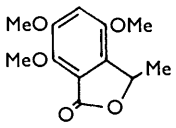
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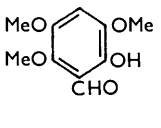
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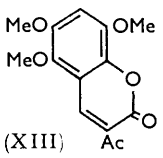
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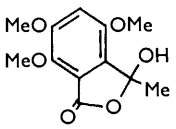
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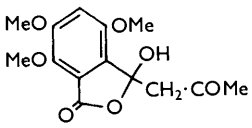
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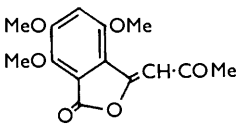
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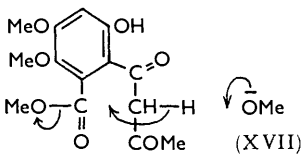
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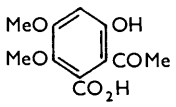
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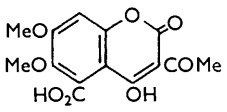
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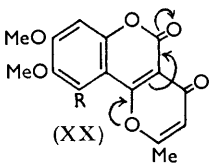
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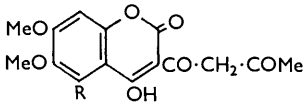
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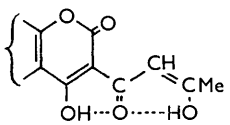
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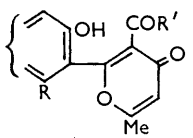
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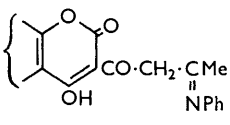
(XXIV)

Permanganate oxidised the aldehyde (X) to the corresponding acid which, like other *o*-acetylbenzoic acids, behaved spectroscopically as the lactol (XIV). In Claisen condensations with methyl acetate and sodium methoxide, this lactol provided a β-diketone which gave a ferric reaction but, on spectroscopic grounds, must also be allocated a lactol structure (XV). Attempts to convert this β-diketone into an acetylindanedione by inducing an internal Claisen reaction with sodium hydride or sodium hydroxide failed, but when the β-diketone was converted into the acetonylidenephthalide (XVI) by thermal dehydration and then treated with sodium methoxide a smooth transformation into the desired product (VI; R = Me) occurred. This was identical with the methyl ether of the degradation product, which is therefore correctly represented as (VI; R = H).

Because Schwerin [6] maintained that the cyclisation of *o*-acetoacetylbenzoic acids to

[6] Schwerin, *Ber.*, 1894, **27**, 104; see Horton and Murdock, *J. Org. Chem.*, 1960, **25**, 938, for further references.

acetylindanediones is spontaneous, it was suggested that the hydrolytic degradation of citromycetin [2] and fulvic acid [5] derivatives to the indanedione (VI; R = H) occurred by way of the carboxylic acid (III; R = H). This view can no longer be maintained because in this series at least * such acids did not cyclise thus and the efficacy of sodium methoxide alone amongst the bases examined strongly suggests that the essential reaction is the extrusion of methoxide ion from the ester group by the acetoacetyl carbanion as indicated in (XVII). The alkaline hydrolysis of methyl di-*O*-methylcitromycetinone (I; R = Me) has been investigated anew with this point in mind.

Alkali can attack methyl di-*O*-methylcitromycetinone (I; R = Me) at the methoxycarbonyl group and at the pyrone rings, the nature of the products depending on the relative rates. It would be expected that, in so far as the ester group survives, the β-diketone (XVII) would be formed and hence the acetylindanedione which is stable to further attack by bases. If this ester group does not survive, then the β-diketonic carboxylic acid (III) would be produced but would suffer further hydrolysis. In our experience, 2N-sodium hydroxide converts methyl di-*O*-methylcitromycetinone, not only into the acetylindanedione (VI; R = H) in the way described by other workers, but also into the acid (XVIII) not detected previously. The structure of this acid has been confirmed by synthesis (see following paper) and can be regarded as resulting from hydrolysis of acid (III; R = H) as predicted. Moreover, the properties of this acid are in every way identical with those described [3] for the Hetherington–Raistrick " pyrone " except for the analytical data: in spite of this discrepancy we consider that their " pyrone " must have been the acid (XVIII).

The kindness of Dr. W. B. Whalley in providing us with specimens derived from earlier work on citromycetin has allowed us to clarify some other details of the chemistry of this compound. When hydrolysed by 0·5N-sodium hydroxide, methyl di-*O*-methylcitromycetinone (I; R = Me) furnishes the corresponding acid (I; R = H) that is reconverted into the parent ester by diazomethane. The production of this acid had not been recognised in the earlier studies, but it is identical with a hydrolysis product formerly considered to be the coumarin (XIX). In consequence, the observation by Robertson, Whalley, and Yates [2] that the coumarin (XIX) gives very little of the chromone (II) when treated with alkali can now be translated into evidence that the acid (I; R = H) gives very little of the acetylindanedione (VI; R = H): this accords entirely with the present views as to the source of the last-mentioned compound.

Finally, hydrolysis of methyl di-*O*-methylcitromycetinone (XX; R = CO_2Me) by hydrochloric acid had been shown to give the β-diketonic α-pyrone (XXI; R = CO_2Me), whereas hydration on a palladium catalyst had been considered [7] to yield the isomeric γ-pyrone (XXIII; R = CO_2Me, R′ = OH). Similarly, hydrolysis of di-*O*-methylcitromycinone (XX; R = H) had been shown to yield (XXI; R = H), but hydration on a catalyst was considered to give (XXIII; R = H, R′ = OH). Materials obtained by the second method appeared to have properties very similar to those obtained by the first, and in fact specimens prepared by the two methods are spectroscopically identical. The infrared spectrum of compound (XXI; R = H), as a Nujol mull, shows no discrete hydroxylic bands, and no ketonic bands higher than 1600 $cm.^{-1}$, whereas absorption at 1724 $cm.^{-1}$ must be attributed to an α-pyrone ring. Thus there is evidence that the hydrolysis products are of type (XXI) and not of type (XXIII) and that the β-diketones (XXI) exist as hydrogen-bonded enols (XXII). The anilides of type (XXIII; R′ = NHPh) can now be re-formulated as the anils (XXIV), a revision which accounts equally well for their formation from aniline and either the γ-pyrones (XX) or the β-diketones (XXI). This revision is satisfactory on theoretical grounds also, for the electronic interaction indicated in (XX) would reduce the reactivity of the lactonic-carbonyl group to

* The examples given by Schwerin have not been re-examined.

[7] Cavill, Robertson, and Whalley, *J.*, 1950, 1031; Whalley, in " Progress in Organic Chemistry," ed. Cook, Butterworths Scientific Publishers, London, 1958, Vol. IV, p. 72.

bases below that normally found in coumarins, but would much increase that of the γ-pyrone ring.

Experimental

Attempted Methylation of 2-Acetylindane-1,3-dione.—(*a*) When this indanedione (1·0 g.) in boiling acetone (80 ml.) containing potassium carbonate (1·5 g.) and methyl iodide (1 ml.) was treated with further portions (0·3 ml.) of methyl iodide every 3 hr. for 24 hr. some reaction occurred. The product was isolated by evaporating the filtered solution and triturating the residue with saturated aqueous sodium hydrogen carbonate. 2-Acetylindane-1,3-dione (0·6 g.) was recovered by acidification of the orange solution: crystallisation of the colourless residue from benzene–light petroleum (b. p. 60—80°) gave an unidentified substance in the form of plates (0·13 g.), m. p. 190° (Found: C, 75·1; H, 4·5%).

(*b*) The indanedione (0·5 g.) was converted into the sodium salt by the requisite quantity of 2N-sodium hydroxide and when treated with 0·1N-silver nitrate in excess furnished a silver salt. This was washed with water, dried *in vacuo* in the dark, suspended in benzene (10 ml.), and heated with methyl iodide (1 ml.) for 1 hr. The yellow solution was filtered and on evaporation left a brown oil which was dissolved in benzene and washed with aqueous sodium hydrogen carbonate. The neutral material recovered from the benzene crystallised from aqueous methanol, giving yellow plates m. p. 133°. It rapidly decomposed when kept and failed to yield methyl iodide in Zeisel determinations.

2-Acetyl-4,5,7-trimethoxyindane-1,3-dione (VI; R = Me).—(*a*) Obtained by degradation of fulvic acid,[5] 2-acetyl-7-hydroxy-4,5-dimethoxyindane-1,3-dione (VI; R = H) (0·5 g.) was treated in boiling 5% aqueous sodium hydroxide with methyl sulphate (1 ml.) added gradually during 1 hr. A bright yellow sodium salt slowly separated, and this was collected, suspended in water, and decomposed by being shaken with dilute hydrochloric acid. The remaining solid was still yellow, and when collected and crystallised from methanol afforded the *trimethoxyindanedione* in golden needles (0·3 g.), m. p. 175—176° [Found: C, 60·4; H, 5·3; OMe, 33·3. $C_{11}H_5O_3(OMe)_3$ requires C, 60·4; H, 5·1; OMe, 33·5%]. This compound was soluble in sodium hydrogen carbonate solutions and gave a reddish-brown ferric reaction. It had $\lambda_{max.}$ (in EtOH) 289, 299 mμ (log ε 4·45, 4·45) and (in Nujol) $\nu_{max.}$ 1711, 1643, 1631, and 1605 cm.$^{-1}$: these values compare closely with those of the parent phenol.[5]

This methyl ether (0·15 g.) was oxidised in boiling acetone (15 ml.) by powdered potassium permanganate (0·75 g.) added in small portions during 1·5 hr. After a further ½ hr. at the b. p. the mixture was clarified by addition of water (5 ml.) and passage of a stream of sulphur dioxide. The aqueous solution left after filtration and removal of the acetone was extracted continuously with ether for 3 hr., and the acidic fraction was isolated from the extract by means of sodium hydrogen carbonate. The product, a brown gum, was purified by sublimation at 140°/0·1 mm. The pale green crystalline sublimate (5 mg.) was recrystallised from ethyl acetate–light petroleum (b. p. 60—80°), giving 3,4,6-trimethoxyphthalic anhydride in needles, m. p. and mixed m. p. 210—211°.

(*b*) The acetonylidenephthalide (XVI) (0·05 g.) (see below) was kept in methanol (10 ml.) containing sodium methoxide (0·01 g.) for 12 hr. A yellow sodium salt separated, and this was dissolved in water (5 ml.) and acidified with hydrochloric acid, giving the trimethoxyindanedione which crystallised from methanol in golden needles, m. p. 175—176°, not depressed by admixture with a specimen prepared as in (*a*) above. Samples prepared by methods (*a*) and (*b*) had identical infrared spectra.

2-Acetyl-3,5,6-trimethoxybenzaldehyde (X).—Ozonised oxygen was bubbled through water and then through a solution of 3,4,6-trimethoxy-2-propenylacetophenone [1] (1 g.) in ethyl acetate (20 ml.) at −70°. Separation of a white solid began after about ½ hr., and was complete after 1 hr. This solid crystallised from benzene–light petroleum (b. p. 60—80°), giving the *2-acetylbenzaldehyde* in rosettes of pinkish needles (0·6 g.), m. p. 121—122°, $\lambda_{max.}$ (in EtOH) 223, 272, 339 mμ (log ε 4·14, 3·60, 3·29), $\nu_{max.}$ 1681, 1639, and 1590 cm.$^{-1}$ [Found: C, 60·4; H, 6·0; OMe, 36·2; *C*-Me (Kuhn–Roth), 5·0. $C_9H_5O_2(OMe)_3$ requires C, 60·5; H, 5·9; OMe, 39·1; 1*C*-Me, 6·3%]. This aldehyde rapidly became red when exposed to air. From the mother-liquors a small quantity of the iso-ozonide, m. p. and mixed m. p. 116°, was isolated.

The *aldoxime*, m. p. 212—214° (decomp.) (Found: C, 56·4; H, 5·8; N, 5·5. $C_{12}H_{15}NO_5$ requires C, 56·9; H, 6·0; N, 5·5%), separated from a solution of the aldehyde (0·2 g.), hydroxylamine hydrochloride (0·5 g.), and sodium acetate (0·2 g.) in alcohol (4 ml.) and water (4 ml.). As it did not crystallise from organic solvents it was purified by repeated precipitation from solutions of its sodium salt by acids. Its unusual properties (reddish-violet ferric reaction and lack of intense absorption in the carbonyl region of the infrared spectrum) are consistent with earlier work on this type of compound.[8]

4,6,7-*Trimethoxy*-3-*methylphthalide* (XI).—When the foregoing aldehyde (0·5 g.) was added in small portions to N-aqueous sodium hydroxide (20 ml.) and shaken it dissolved slowly. The solution was cooled in ice and the product, liberated by dilute hydrochloric acid, was purified from methanol, giving the *phthalide* as needles (0·3 g.), m. p. 140—141°, $\nu_{max.}$ 1764, 1610 cm.$^{-1}$ [Found: C, 60·3; H, 6·0; OMe, 39·3; *C*-Me (Kuhn–Roth), 6·3. $C_9H_5O_2(OMe)_3$ requires C, 60·5; H, 5·9; OMe, 39·1; 1*C*-Me, 6·3%]. This compound, though neutral, dissolved in alkaline media and was recovered by acidification.

2-*Hydroxy*-3,5,6-*trimethoxybenzaldehyde* (XII).—To the foregoing aldehyde (1·5 g.) in methyl acetate (50 ml.) was added a 5% solution (8·5 ml.) of performic acid in formic acid. After 1·5 hr. at 20° and then 0·5 hr. at 90° the cooled mixture was diluted with ether (100 ml.) and extracted with 2N-sodium hydroxide. Acidification of the extract gave crystals which, when recrystallised from light petroleum (b. p. 60—80°), furnished the 2-*hydroxybenzaldehyde* in yellow needles (0·7 g.), m. p. 84° [Found, on specimen dried *in vacuo* at 60°: C, 56·6, 56·7; H, 6·0, 5·7; OMe, 43·6, 43·9. $C_7H_3O_2(OMe)_3$ requires C, 56·6; H, 5·7; 3OMe, 43·9%]. Kuhn–Roth estimations showed that no *C*-methyl groups were present.

A mixture of this salicylaldehyde (0·25 g.) and ethyl acetoacetate (5 ml.) containing a little piperidine slowly solidified. The solid was purified from ethyl acetate; it gave 3-*acetyl*-5,6,8-*trimethoxycoumarin* (XIII) as orange needles (0·12 g.), m. p. 165—166° [Found, on specimen dried *in vacuo* at 110°: C, 60·2; H, 5·2; OMe, 33·3. $C_{11}H_5O_3(OMe)_3$ requires C, 60·4; H, 5·1; OMe, 33·5%], $\nu_{max.}$ 1718 (coumarin C:O) and 1669 cm.$^{-1}$ (αβ-unsaturated ketone).

2-*Acetyl*-3,5,6-*trimethoxybenzoic Acid*.—2-Acetyl-3,5,6-trimethoxybenzaldehyde (2 g.) in acetone (100 ml.) at the b. p. was oxidised by a solution of potassium permanganate (5 g.) and magnesium sulphate (5 g.) in water (100 ml.) added in 3 min. The solution was decolorised by a stream of sulphur dioxide, freed from acetone by distillation, and extracted with chloroform (3 × 50 ml.). From the extracts the desired *acetylbenzoic acid* was isolated by means of aqueous sodium carbonate and crystallised from aqueous alcohol as prisms (0·8 g.), m. p. 180° [Found: C, 56·6; H, 5·7; OMe, 36·6. $C_9H_5O_3(OMe)_3$ requires C, 56·7; H, 5·6; OMe, 36·6%]. Infrared absorption in Nujol mulls ($\nu_{max.}$ 3470, 1748, and 1618 cm.$^{-1}$) suggested that, in the solid state, this acid exists as the lactol (XIV), but the compound was readily soluble in aqueous sodium hydrogen carbonate.

This acid (0·5 g.) was also prepared by oxidising the propenylacetophenone (VIII) (4 g.) in the same way.

2-*Acetoacetyl*-3,5,6-*trimethoxybenzoic Acid*.—Attempts to effect Claisen condensations between the *o*-acetylbenzoic acid (XIV) and methyl acetate by means of sodium methoxide failed when the solvent used was benzene or dioxan. To the acetylbenzoic acid (0·8 g.) in tetrahydrofuran (30 ml.) was added freshly prepared sodium methoxide (2 g.). The mixture was kept at the b. p. for ½ hr. while methyl acetate (2 ml.) diluted by tetrahydrofuran (20 ml.) was run in gradually. After 3 hr. at the same temperature the mixture had deposited a fine yellow powder which was collected, dissolved in iced water, and acidified with hydrochloric acid. The product separated slowly and was crystallised from methanol, giving the *o-acetoacetylbenzoic acid* in plates (0·6 g.), m. p. 167—168° (decomp.) [Found: C, 56·5, 56·8; H, 5·4, 5·7; OMe, 31·6, 31·6; *C*-Me (Kuhn–Roth), 5·2. $C_{11}H_7O_4(OMe)_3$ requires C, 56·8; H, 5·4; OMe, 31·4; 1*C*-Me, 5·1%]. Though this diketone is soluble in aqueous sodium hydrogen carbonate and gives in alcohol a blood-red ferric reaction, the spectroscopic data [$\lambda_{max.}$ (in EtOH) 326 mμ (log ε 3·80); $\nu_{max.}$ 3390 (OH), 1754 (phthalide C:O), 1715 (saturated ketone), and 1613 cm.$^{-1}$] suggest that in the solid state it is present as the lactol (XV).

Heated with 2N-sodium hydroxide (2·5 ml.) on the steam-bath for ½ hr., the β-diketone (0·1 g.) gave an orange solution from which acidification precipitated 2-acetyl-3,5,6-trimethoxybenzoic acid, forming prisms (0·07 g.), m. p. and mixed m. p. 180°, from alcohol.

[8] Griffiths and Ingold, *J.*, 1925, **127**, 1698.

3-*Acetonylidene*-4,6,7-*trimethoxyphthalide* (XVI).—The sublimate obtained when the foregoing β-diketone (0·1 g.) was kept at 200°/0·4 mm. for 15 min. was crystallised from methanol, giving the *acetonylidenephthalide* in long yellow prisms, m. p. 219—220°, $\lambda_{max.}$ (in EtOH) 232, 270, 387 mμ (log ε 4·22, 4·22, 4·18), $\nu_{max.}$ (Nujol) 1783 (3-alkylidenephthalide), 1757sh, 1678 (αβ-unsaturated ketone), and 1603 cm.$^{-1}$ [Found: C, 60·2; H, 5·1; OMe, 32·8, 33·0; *C*-Me (Kuhn–Roth), 4·7. $C_{11}H_5O_3(OMe)_3$ requires C, 60·4; H, 5·1; OMe, 33·4; 1*C*-Me, 5·4%].

The same compound was also produced during an attempt to convert the β-diketone (XV) into an acetylindanedione. This β-diketone (0·1 g.) was heated with sodium hydride (0·05 g.) in boiling pyridine (5 ml.) for 15 min. The cooled solution was treated with a little acetic acid to destroy residual sodium hydride, and then poured into an excess of ice-cold acetic acid. The product was extracted into chloroform, recovered by evaporation, and crystallised from methanol to furnish the acetonylidenephthalide (0·06 g.), m. p. and mixed m. p. 219—220°.

Alkaline Hydrolysis of Methyl Di-O-methylcitromycetinone.—(a) 2N-*Sodium hydroxide.* The orange solution obtained by boiling methyl di-*O*-methylcitromycetinone (1·0 g.) with 2N-aqueous sodium hydroxide (50 ml.) for ½ hr. was acidified with 2N-sulphuric acid. The yellow precipitate was collected and when crystallised from methanol furnished 2-acetyl-7-hydroxy-4,5-dimethoxyindane-1,3-dione in needles (0·25 g.), m. p. 157°. Extraction of the filtrate with ether resulted in an orange solution which deposited a white solid after partial concentration: evaporation of the filtrate from the white solid supplied a further quantity (0·07 g.) of the indanedione.

Purified from methanol, the white solid gave 2-*acetyl*-3-*hydroxy*-5,6-*dimethoxybenzoic acid* (XVIII) which formed prisms (0·02 g.), m. p. 181° (decomp.), having a green ferric reaction in alcohol but a purplish-brown ferric reaction in aqueous alcohol [Found: C, 55·3; H, 5·1; OMe, 26·0. $C_9H_6O_4(OMe)_2$ requires C, 55·0; H, 5·0; OMe, 25·8%]. Further details of its properties and a synthesis are recorded in the following paper.

(b) 0·5N-*Sodium hydroxide.* When the orange solution obtained by heating methyl di-*O*-methylcitromycetinone (1·0 g.) with 0·5N-aqueous sodium hydroxide (50 ml.) on the steam-bath for 1 hr. was acidified, ether-extraction removed from it a little 2-acetyl-7-hydroxy-4,5-dimethoxyindane-1,3-dione (0·05 g.). When the extracted solution was kept, an ether-insoluble solid gradually separated and was purified from a large volume of methanol. Obtained thus, *di-O-methylcitromycetinone* (I; R = H) formed long needles (0·2 g.), m. p. 314° (decomp.) (Found, on specimen dried at 140° *in vacuo* for 8 hr.: C, 57·4; H, 3·9. $C_{16}H_{12}O_8$ requires C, 57·8; H, 3·6%). This acid had $\nu_{max.}$ (in Nujol) 3610, 3472, 3367 (partially bonded OH of CO_2H), 1754 (α-pyrone C:O), 1695 (carboxyl C:O), 1661 (γ-pyrone C:O), 1623, and 1597 cm., and was identified by mixed fusion and spectroscopically with a specimen of the substance prepared by Robertson, Whalley, and Yates [2] and regarded by them as the 3-acetylcoumarin (XIX). Diazomethane rapidly reconverted this acid into methyl di-*O*-methylcitromycetinone, m. p. and mixed m. p. 240°, further identified spectroscopically.

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