486. *Condensation Products of Maleic Anhydride with Phenols.*

By K. P. Barr, F. M. Dean, and H. D. Locksley.

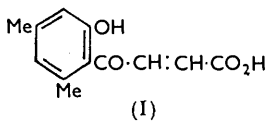
The condensation of maleic anhydride with phenols or the related cyclisation of β-2-hydroxybenzoylacrylates gives derivatives of chromanone, whereas 3 : 5-xylenol gives a coumaranone, a variation thought to have a steric origin. A revised structure is suggested for the dimer obtained when methyl β-2-hydroxy-3 : 5-dimethylbenzoylacrylate is treated with bases.

Apart from the hydrogenation [1,2] of chromone-2-carboxylates, the published syntheses [1,3,4] of chromanone-2-carboxylates are ambiguous; the possibility that the isomeric coumaranonylacetates might be formed seems not to have been discussed. Of the five reactions considered here, four did give chromanones but, in contrast to an earlier report,[3] one gave a coumaranone.

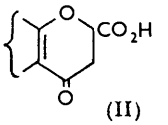
Condensation of maleic anhydride with 3 : 5-xylenol in Friedel–Crafts conditions furnished Baddeley, Makar, and Ivinson [3] with two isomeric acids, one yellow and one

[1] Jarowski, Moran, and Cramer, *J. Amer. Chem. Soc.*, 1949, **71**, 944.
[2] Cramer, Schroeder, Moran, Nield, Edwards, Jarowski, and Puetzer, *J. Amer. Pharm. Assoc.*, 1948, **37**, 439.
[3] Baddeley, Makar, and Ivinson, *J.*, 1953, 3969.
[4] Cocker, Hayes, and Williamson, *J.*, 1955, 824.

colourless, to which structures (I) and (II) were allocated. Aluminium chloride at 130° transformed the yellow into the colourless isomer, which was also produced by the action of sulphuric acid on the phenoxysuccinic acid (III). Clearly, these reactions do not define the size of the heterocyclic ring in (II).



(I)



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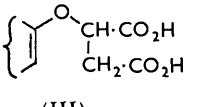

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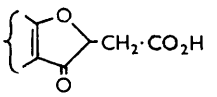
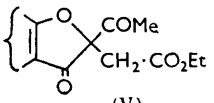


(IV)



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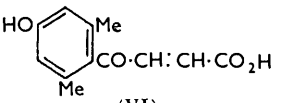
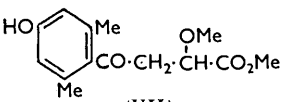
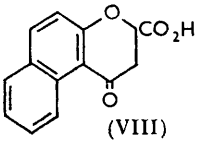


(VI)



(VII)



(VIII)

Repetition of the work of Baddeley *et al.* furnished us with the same two acids, of which the colourless one was identical with the product (IV) from acid hydrolysis [5] of the authentic coumaranone (V). Because hydrolysis might have involved a β-elimination leading to the acrylic acid (I) which could then form a chromanone, this sequence does not establish structure (IV) unequivocally: for similar reasons (cf. refs. 1 and 2) no attempts were made to define by chemical methods the ring-size of any compounds of types (II) and (IV). As it seemed that spectroscopic differences [5,6] between the two types in the ultraviolet and the carbonyl-stretching region would be small, potentiometric titration [7] appeared to provide the most reliable criterion. In this, the colourless isomer behaved as a propionic acid rather than as an α-phenoxy-acid so that structure (IV) is the correct one. This conclusion is supported by the ease with which the methyl ester is oxidised by air (a reaction [5] typical of coumaranones with one hydrogen atom in the 2-position), and by the negative Zimmermann reaction. The decarboxylation product described by Baddeley *et al.* is therefore probably 2 : 4 : 6-trimethylcoumaranone and not 5 : 7-dimethylchromanone.

Attempts to cyclise the yellow isomer to the coumaranone (IV) under conditions milder than those used by the previous investigators failed. With acidified methanol this acid formed an ester containing an additional methoxyl group and having an ultraviolet spectrum characteristic of a *p*-hydroxyacetophenone. Further, this ester absorbed selectively, not only at 1730 cm.$^{-1}$ (ester), but also at 3390 (OH) and 1695 cm.$^{-1}$ (acetophenone C:O), thus contrasting with authentic *o*-hydroxyacetophenones.[8] Finally, neither the yellow acid nor the methoxy-ester responded to the ferric test, so this acid is not (I) but (VI), and the methoxy-ester is (VII). Cyclisation of the yellow acid (VI) to the coumaranone (IV) must therefore be preceded by a migration usual in Friedel–Crafts conditions.

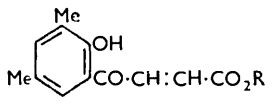
Unlike 3 : 5-xylenol, β-naphthol gave but one product. This had a negative ferric reaction, gave with diazomethane a non-phenolic ester responding to the Zimmermann test for active methylene,* and behaved in potentiometric titration as an α-phenoxy-acid. It is therefore considered to have structure (VIII).

With maleic anhydride and aluminium chloride, 2 : 4-xylenol gave the β-aroylacrylic acid (IX; R = H) which is stable to acids and bases. The cyclisation of the derived

* Authentic 2-methylchromanones give this test, but flavanones do not, presumably because of the ease with which the heterocyclic ring opens in the latter.

[5] Dean and Manunapichu, *J.*, 1957, 3112.
[6] Jarowski and Hess, *J. Amer. Chem. Soc.*, 1949, **71**, 1711.
[7] Brown, McDaniel, and Häfliger in " Determination of Organic Structures by Physical Methods," ed. Braude and Nachod, Academic Press, New York, p. 567.
[8] Bellamy, " The Infra-Red Spectra of Complex Molecules," Methuen, London, 1958.

methyl ester has been studied by Cocker, Hayes, and Williamson,[4] who found that triethylamine in alcohol containing ethyl malonate furnished a monomer formulated as the chromanone (X; R = Me): omission of the malonate led to a dimer formulated as the diacylethylene (XI). In our experiments mixtures of the monomer and the dimer resulted whatever the conditions of cyclisation, but fractional crystallisation supplied products identical with specimens kindly provided by Dr. W. R. N. Williamson. When hydrolysed by hydrobromic acid, the monomer gave a product (X; R = H) corresponding to that obtained by Cocker *et al.* by treatment of 2 : 4-xylyl hydrogen maleate with aluminium



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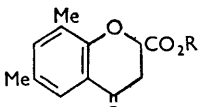
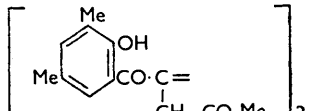
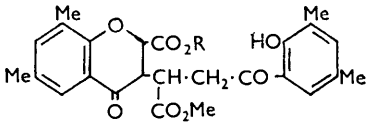


(X)



(XI)



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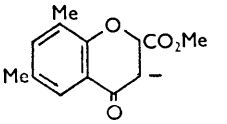

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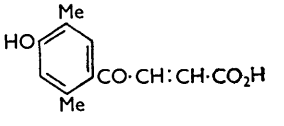

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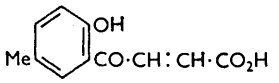

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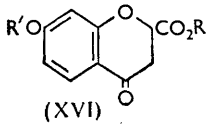
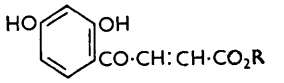


(XVI)



(XVII)

chloride and having an acidity which indicated the presence of a chromanone-2-carboxylic acid grouping: as the monomer was regenerated by alkylation with diazomethane and responded to the Zimmermann reagent, structure (X) holds good. For the dimer, however, structure (XII; R = Me) is preferable to structure (XI) because (i) the ultraviolet spectrum [4] corresponds to that of the chromanone (X) together with the corresponding *o*-hydroxyacetophenone rather than to that expected from a compound with more extended conjugation [the dimer is faintly yellow and not orange like (IX)], (ii) acetylation and methoxyacetylation gave, not diacyl derivatives, but monoacyl derivatives transparent near 3 μ, and (iii) partial hydrolysis gave an acid (XII; R = H) which regenerated the dimer with diazomethane and behaved as a chromanone-2-carboxylic acid in potentiometric titration. The carbanion (XIII) would be the initial product of base-catalysed cyclisation and in competitive protonation and Michael addition with unchanged β-aroylacrylate (IX; R = Me) would give the chromanone (X) and the dimer (XII). The expectation that with ethanolamine as the catalyst the proportion of monomer would increase (the catalyst itself being able to supply the proton required at the 3-position) was not realised although this catalyst was by far the most effective studied. Similar Michael additions have been observed by Padfield and Tomlinson.[9]

From 2 : 5-xylenol only the acid (XIV) was obtained, so that cyclisations in this series could not be studied: the methyl ester of the acid (XV) from *p*-cresol gave with triethylamine a dimer closely similar to that from (IX) but no monomer.

Resorcinol gave both the chromanone-2-carboxylic acid (XVI; R = R' = H) and the acrylic acid (XVII; R = H). The former had the ultraviolet absorption of resacetophenone and in potentiometric titration showed inflections appropriate to the carboxyl group and the *p*-hydroxyacetophenone system. Diazomethane supplied first the phenolic ester (XVI; R = Me, R' = H) and then the neutral methoxy-ester (XVI; R = R' = Me) which gave a positive Zimmermann reaction. The methyl ester (XVII; R = Me), when

[9] Padfield and Tomlinson, *J.*, 1950, 2272.

treated with potassium carbonate and later with methyl iodide, furnished a complex mixture containing but little of the chromanone (XVI; R = R′ = Me).

These results indicate that the single example of coumaranone formation is not to be explained electronically. For example, even in the resorcinol series in which the carbonyl group is deactivated by two hydroxyl groups (or anions in basic media), a chromanone and not a coumaranone is formed. Well known in 2-methylacetophenones and related systems,[11,12] steric interference between the carbonyl and methyl groups would be accentuated in complexes and could account for the formation of the coumaranone (IV) in which these groups are drawn apart and would therefore interfere less. The methine group at the 5-position of (VIII) is apparently too small to exert this effect.

It is concluded that cyclisations of the kind considered here give chromanones unless these would carry bulky substituents in the 5-position, in which case coumaranones may be formed.

Experimental

Ultraviolet spectra were determined for ~10^{-3}M-alcoholic solutions by means of a Unicam S.P. 300 spectrophotometer. Infrared spectra refer to Nujol mulls and were determined by means of a Perkin-Elmer infrared spectrophotometer Model 21. Potentiometric titrations against 0·005N-sodium hydroxide were effected in 50% alcohol: the results were corrected to pK_a(H_2O) by means of the corresponding values for benzoic acid.

4 : 6-*Dimethyl*-2-*coumaranonylacetic acid* (IV) *and* β-4-*Hydroxy*-2 : 6-*dimethylbenzoylacrylic Acid* (VI).—Maleic anhydride and 3 : 5-xylenol in ethylene chloride were treated with aluminium chloride, and the acidic products were separated as described by Baddeley *et al.*[3] The same products were obtained with tetrachloroethane as solvent, but in carbon disulphide only the colourless acid was formed. The colourless acid, 4 : 6-dimethyl-2-coumaronylacetic acid, separated from dilute alcohol in needles, m. p. **143—144°**, undepressed on admixture with a specimen prepared [5] from the coumaranone (V) (Found: C, 65·5; H, 5·4. Calc. for $C_{12}H_{12}O_4$: C, 65·4; H, 5·5%). This acid had pK_a 4·75 and $\lambda_{max.}$ 263 and 328 mμ (log ε 4·08, 3·77). The *methyl ester* (prepared by use of diazomethane) crystallised in needles, m. p. 60—61°, $\lambda_{max.}$ 265 and 328 mμ (log ε 4·12, 3·68), but resinified in air (Found: C, 66·7; H, 5·9. $C_{13}H_{14}O_4$ requires C, 66·6; H, 6·0%). For the ester obtained from their acid and methanolic hydrogen chloride, Baddeley *et al.* give m. p. 67—68°.

The yellow acid, β-4-*hydroxy*-2 : 6-*dimethylbenzoylacrylic acid* (VI), crystallised from dilute acetic acid in prisms, m. p. 186° (Baddeley *et al.*[3] give m. p. 186—187° for their product), devoid of a ferric reaction (Found: C, 65·2; H, 5·4. $C_{12}H_{12}O_4$ requires C, 65·4; H, 5·5%). The orange solution of this acid (1·0 g.) in boiling methanol (50 ml.) containing sulphuric acid (0·5 ml.) faded in 1 hr. and on dilution followed by crystallisation of the product from aqueous methanol gave *methyl* β-4-*hydroxy*-2 : 6-*dimethylbenzoyl*-α-*methoxypropionate* (VII) in prisms, m. p. 115°, $\lambda_{max.}$ 274 mμ (log ε 4·55), soluble in 2N-sodium hydroxide but not in 2N-sodium carbonate [Found: C, 62·9; H, 6·9; OMe, 22·7. $C_{12}H_{12}O_3(OMe)_2$ requires C, 63·1; H, 6·8; OMe, 23·3%].

5 : 6-*Benzochromanone*-2-*carboxylic Acid* (VIII).—During ¾ hr., β-naphthol (36 g.) in nitrobenzene (150 ml.) was added to aluminium chloride (66 g.) and maleic anhydride (24 g.) in stirred nitrobenzene (150 ml.). After 36 hr., the complex was decomposed by ice and concentrated hydrochloric acid, and the solvent was removed by steam-distillation. The residual red oil crystallised from benzene, giving 5 : 6-*benzochromanone*-2-*carboxylic acid* in needles (21 g.), m. p. 169°, pK_a 3·95, devoid of a ferric reaction (Found: C, 69·4; H, 4·0%; equiv., 230. $C_{13}H_9O_2{\cdot}CO_2H$ requires C, 69·4; H, 4·1%; equiv., 242). The *methyl ester* (prepared by means of diazomethane) separated from light petroleum (b. p. 40—60°) in plates, m. p. 102—103°, giving a red Zimmermann reaction (Found: C, 69·9; H, 5·0. $C_{15}H_{12}O_4$ requires C, 70·2; H, 4·7%).

[10] Kirchner, Baily, and Cavallito, *J. Amer. Chem. Soc.*, 1949, **71**, 1210.
[11] Waight and Erskine in " Steric Effects in Conjugated Systems," ed. Gray, Butterworths, 1958.
[12] Conover, " Symposium on Antibiotics and Mould Metabolites," p. 48, Chemical Society Special Publication No. 5 (1956).

Methyl 6 : 8-*Dimethylchromanone*-2-*carboxylate* (X; R = Me) *and Methyl* β-(2-*Hydroxy*-3 : 5-*dimethylbenzoyl*)-α-(2-*methoxycarbonyl*-6 : 8-*dimethylchromanon*-3-*yl*)*propionate* (XII; R = Me).—When the red colour of a solution of methyl β-2-hydroxy-3 : 5-dimethylbenzoylacrylate (0·5 g.) in methanol (100 ml.) containing triethylamine (0·1 ml.) had faded, dilution with 2N-hydrochloric acid (300 ml.) gave a gum. Crystallised from methanol, this product supplied the *ester* (XII; R = Me) in prisms (0·3 g.), m. p. 144°, $\nu_{max.}$ 1748 (ester), 1715 (chromanone-carbonyl), and 1642 cm.$^{-1}$ (chelated acetophenone-carbonyl) [Found: C, 66·4; H, 5·8; OMe, 13·0%; *M* (Rast), 421. $C_{24}H_{22}O_6(OMe)_2$ requires C, 66·7; H, 6·0; OMe, 13·2%; *M*, 468]. The *acetate* (obtained by use of acetic anhydride and perchloric acid) crystallised from methanol in prisms, m. p. 120°, with a negative ferric reaction [Found: C, 65·6; H, 5·9; OMe, 12·2, 12·0. $C_{26}H_{24}O_7(OMe)_2$ requires C, 65·9; H, 5·9; OMe, 12·1%]. The *methoxyacetate* (prepared by use of methoxyacetyl chloride in pyridine initially at −50° to avoid charring) separated from methanol in needles, m. p. 123° [Found: C, 64·2, 64·5; H, 6·1, 6·1; OMe, 16·7. $C_{26}H_{23}O_7(OMe)_3$ requires C, 64·4; H, 6·0; OMe, 17·2%].

From the mother-liquors of the " dimeric " ester (XII; R = Me), methyl 6 : 8-dimethylchromanone-2-carboxylate (X; R = Me) separated in hexagonal rods (0·15 g.), m. p. 100°, $\nu_{max.}$ 1736 (ester) and 1712 cm.$^{-1}$ (chromanone-carbonyl), giving a purple Zimmermann reaction (Found: C, 66·5; H, 5·7. Calc. for $C_{13}H_{14}O_4$: C, 66·7; H, 6·0%). This and the foregoing compound were identified by mixed melting point and spectroscopic methods with specimens provided by Dr. W. R. N. Williamson.

A cursory examination of other conditions for this cyclisation showed that (i) the acrylate (IX; R = Me) gave a red solution in triethylamine but was recovered after some hours by rapid neutralisation of the base, (ii) pyridine did not induce cyclisation, (iii) potassium carbonate, triethylamine, hydrazine, and ethanolamine were effective catalysts in methanol or water, (iv) in dioxan or tetrahydrofuran the effectiveness of triethylamine was low unless water or methanol was added, (v) ethanolamine was a very active catalyst in all solvents examined, and (vi) addition of ethyl malonate and other variations in the conditions (*e.g.*, temperature, dilution) had little or no effect on the relative yields of the products.

The ester (XII; R = Me) was unchanged when kept in methanol with triethylamine; but when methyl 6 : 8-dimethylchromanone-2-carboxylate (95 mg.) in methanol (100 ml.) containing triethylamine (0·1 ml.) was kept overnight, the solution diluted with 2N-sulphuric acid (200 ml.), and the product crystallised from methanol, the ester (XII; R = Me) (35 mg.), m. p. and mixed m. p. 141°, resulted.

6 : 8-*Dimethylchromanone*-2-*carboxylic Acid* (X; R = H).—The ester (X; R = Me) (150 mg.) was heated on the steam-bath for 15 min. with acetic acid (2 ml.) and hydrobromic acid (*d* 1·5; 1 ml.). Water (50 ml.) and ether (50 ml.) were added: the organic layer was washed with water and extracted with aqueous sodium hydrogen carbonate. Liberated from the extract by concentrated hydrochloric acid and purified from dilute methanol, 6 : 8-dimethylchromanone-2-carboxylic acid formed needles (36 mg.), m. p. 166—170° (decomp.) (Cocker *et al.*[4] give m. p. 170°), pK_a 3·80 (Found: C, 65·2; H, 5·6%; equiv., 228. Calc. for $C_{11}H_{11}O_2{\cdot}CO_2H$: C, 65·4; H, 5·5%; equiv., 220). With diazomethane this acid regenerated the methyl ester, m. p. and mixed m. p. 99°.

α-(2-*Carboxy*-6 : 8-*dimethylchromanon*-3-*yl*)-β-(2-*hydroxy*-3 : 5-*dimethylbenzoyl*)*propionate* (XII; R = H).—The " dimer " (XII; R = Me) (1 g.) was demethylated as in the previous experiment. Repeated crystallisation of the product from methanol gave the 2-*carboxychromanone* in thick triangular prisms (93 mg.), m. p. 196°, $\lambda_{max.}$ 219, 262, and 351 mμ (log ε 4·73, 4·42, 4·01), pK_a 3·73 [Found: C, 66·1, 65·9; H, 5·7, 5·7; OMe, 6·4%; equiv., 427. $C_{23}H_{22}O_5(OMe){\cdot}CO_2H$ requires C, 66·1; H, 5·8; OMe, 6·8%; equiv., 454]. With diazomethane, this acid gave the ester (XII; R = Me), m. p. and mixed m. p. 144°.

β-4-*Hydroxy*-2 : 5-*dimethylbenzoylacrylic Acid* (XIV).—2 : 5-Xylenol (12·2 g.) in tetrachloroethane (75 ml.) was added to a slurry of aluminium chloride (26·8 g.) in the same solvent (100 ml.) cooled in ice. Maleic anhydride (9·8 g.), also in tetrachloroethane (100 ml.), was added during 1 hr. After 3 days, the mixture was treated with ice and 10N-hydrochloric acid (25 ml.), giving a yellow product which was dissolved in a boiling solution of Rochelle salt (200 g.) in water (500 ml.). The filtered solution at 0° deposited crystals from which acidification liberated the *benzoylacrylic acid*. From ethyl acetate this afforded yellow needles (8·7 g.), m. p. 203—205° (decomp.) (Found: C, 65·1; H, 5·6. $C_{12}H_{12}O_4$ requires C, 65·4; H, 5·5%). With methanol and sulphuric acid, this compound gave the *methyl ester*, separating from alcohol

in yellow needles, m. p. 152—154°, devoid of a ferric reaction, unaffected by triethylamine in alcohol, and having $\nu_{max.}$ 3290 (phenolic OH), 1727 (ester), and 1647 cm.$^{-1}$ (conjugated C:O) (Found: C, 66·6; H, 6·0; OMe, 13·2. $C_{12}H_{11}O_3$·OMe requires C, 66·7; H, 6·0; OMe, 13·3%).

Methyl β-(2-Hydroxy-5-methylbenzoyl)-α-(2-methoxycarbonyl-6-methylchromanon-3-yl)-propionate.—Tripropylamine (0·2 ml.) was added to methyl β-2-hydroxy-5-methylbenzoylacrylate [2] (1·05 g.) in alcohol (20 ml.) at 50°. After ½ hr. the solution was cooled in ice. The *product* crystallised in rhombs (0·63 g.), m. p. 128—130°, having a violet-blue ferric reaction (Found: C, 65·2; H, 5·5. $C_{24}H_{24}O_8$ requires C, 65·4; H, 5·5%). The *acetate* (prepared by means of acetic anhydride–sulphuric acid) separated from alcohol in rhombs, m. p. 155—157°, with a negative ferric reaction (Found: C, 64·4; H, 5·7. $C_{26}H_{26}O_9$ requires C, 64·7; H, 5·4%). The cyclisation gave the same results when conducted at −20° or in the presence of ethyl malonate.

7-Hydroxychromanone-2-carboxylic Acid (XVI; R = R′ = H).—Powdered aluminium chloride (120 g.) was slowly added to resorcinol (40 g.) and maleic anhydride (40 g.) in stirred ethylene chloride (1·5 l.). Next day the mixture was warmed to 80° for 1 hr., cooled, and filtered. The yellow residue was decomposed by crushed ice (200 g.) and concentrated hydrochloric acid (100 ml.), and the product was washed with water and fractionally crystallised from 2N-hydrochloric acid. The earlier crops furnished β-2 : 4-dihydroxybenzoylacrylic acid [10] in orange-yellow prisms (10 g.), m. p. 206—208°. Later crops were purified from methanol, giving *7-hydroxychromanone-2-carboxylic acid* in cream prisms (10 g.), m. p. 222° (decomp.), $\lambda_{max.}$ 234, 274, and 316 mμ (log ε 4·08, 4·13, 4·03), pK_a 3·75, 5·35 (Found: C, 57·7; H, 4·0. $C_{10}H_8O_5$ requires C, 57·7; H, 3·9%). The reaction between this acid (1 g.) in tetrahydrofuran (20 ml.) and ethereal diazomethane was stopped after 5 min. by evaporation of the reagent and the solvents. The product in chloroform was purified on a column of silica and then crystallised from benzene, giving *methyl 7-hydroxychromanone-2-carboxylate* (XVI; R = Me, R′ = H) in needles, m. p. 117—118°, which formed a yellow solution in 2N-sodium hydroxide [Found: C, 59·5; H, 4·7; OMe, 14·1%; *M* (Rast), 193. $C_{10}H_7O_4$·OMe requires C, 59·5; H, 4·5; OMe, 14·0%; *M*, 222].

Methyl 7-Methoxychromanone-2-carboxylate (XVI; R = R′ = Me).—(i) Heated in methanol containing sulphuric acid, β-2 : 4-dihydroxybenzoylacrylic acid [10] gave *methyl β-2 : 4-dihydroxybenzoylacrylate* (XVII; R = Me), separating from methanol in yellow needles, m. p. 158°, $\lambda_{max.}$ 230 and 342 mμ (log ε 4·21, 3·97), $\nu_{max.}$ 3330 (OH), 1721 (ester), and 1695 cm.$^{-1}$ (C:O), having a brown ferric reaction in alcohol (Found: C, 59·2; H, 4·6. $C_{11}H_{10}O_5$ requires C, 59·5; H, 4·5%).

This ester (1 g.) in boiling acetone (50 ml.) under nitrogen became red when potassium carbonate (2·5 g.) was added. The colour had faded after 2 hr., but heating was continued for a further 3 hr. The product obtained by dilution of the filtrate with a large excess of cold water was collected into ether, washed with 0·2N-sodium hydroxide, dried (Na_2SO_4), and recovered by evaporation. From the residue, boiling light petroleum (b. p. 60—80°) extracted *methyl 7-methoxychromanone-2-carboxylate*, crystallising from the same solvent in plates (100 mg.), m. p. 66°, which did not respond in the ferric chloride test but gave a cherry-red Zimmermann reaction [Found: C, 60·9; H, 5·1%; *M* (Rast), 234. $C_{12}H_{12}O_5$ requires C, 61·0; H, 5·1%; *M*, 236].

(ii) When the reaction between diazomethane and 7-hydroxychromanone-2-carboxylic acid (0·5 g.) continued for 2 days, the gum produced was purified on silica from benzene, giving the methoxychromanone which formed plates (0·37 g.), m. p. and mixed m. p. 67—68°. This ester had $\lambda_{max.}$ 233, 270, and 319 mμ (log ε 3·98, 4·17, 3·98) and $\nu_{max.}$ 1736 (ester) and 1712 cm.$^{-1}$ (chromanone C:O).

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