317. *Experiments on the Synthesis of Rotenone and its Derivatives. Part XIII.*

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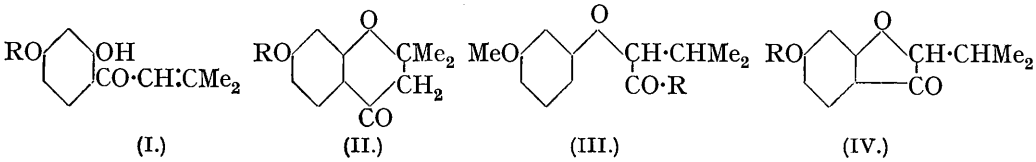
In a search for collateral evidence in support of the structure of 5 : 7-dihydroxychroman the properties of 7-hydroxy-2 : 2-dimethylchromanone and its derivatives have been studied. The synthesis of 6-methoxy-2-*iso*propyl-β-coumaranone by an absolute method confirms the structure of 7-hydroxy-2 : 2-dimethylchromanone and hence that of its reduction product 7-hydroxy-2 : 2-dimethylchroman, which has also been obtained by an independent method.

In forming 2-hydroxy-4-benzyloxyacetophenone on ozonolysis the behaviour of 7-hydroxy-2 : 2 : 4-trimethylchromen, which has been synthesised by two methods, is strictly analogous to that of the natural chromens xanthyletin and xanthoxyletin.

THE experiments described in the present communication were undertaken as an extension of the investigations on the structure and properties of 5 : 7-dihydroxy-2 : 2-dimethylchroman (Part XII, this vol., p. 279) and related compounds, because (*a*) it seemed desirable to obtain collateral evidence in support of the structure of this chroman, and (*b*) the scission of the dihydro-γ-pyrone ring of 5 : 7-dimethoxy-2 : 2-dimethylchromanone with dilute alcoholic sodium hydroxide is of considerable interest in connexion with the stability of the chromanochromanone nucleus present in members of the rotenone series under similar conditions.

According to Arima (*J. Chem. Soc. Japan*, 1932, **53**, 715), 7-hydroxy-2 : 2-dimethylchromanone (II, R = H), prepared by the condensation of resorcinol and ββ-dimethylacryl chloride with aluminium chloride, has a red ferric reaction, but we have found that, although this is true of the partly purified material thus obtained, yet the pure compound is devoid of this property. This chromanone was also obtained when the ββ-dimethylacryl chloride was replaced by β-bromo*iso*valeryl chloride.



(I.) (II.) (III.) (IV.)

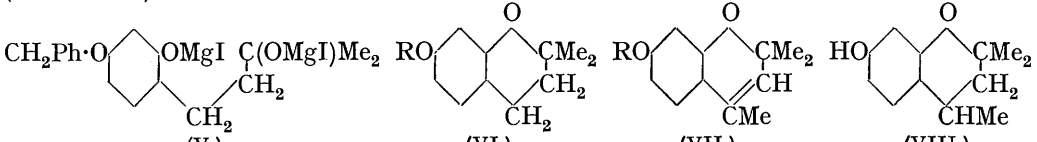
The properties of the chromanone (II, R = H), *viz.*, the negative ferric reaction and the formation of monoacyl and monoalkyl derivatives only, which are insoluble in aqueous sodium hydroxide and do not give ferric reactions, clearly distinguish this compound from the isomeric ketone (I, R = H) but not from the isomeric β-coumaranone (IV, R = H) (compare Arima and Okamoto, *J. Chem. Soc. Japan*, 1929, **50**, 344). The synthesis of the *methyl ether* (IV, R = Me) by an unambiguous method, however, serves to confirm the structure of the coumaranone (IV, R = H) and hence that of the chromanone (II, R = H).

The ether (IV, R = Me) was prepared according to the standard method of Stephen and co-workers (J., 1931, 896) : Interaction of the sodium salt of resorcinol monomethyl ether and ethyl α-bromo*iso*valerate gave rise to the ester (III, R = OEt) mixed with a small amount of ethyl ββ-dimethylacrylate. After hydrolysis of this mixture the *acid* (III, R = OH) was conveniently isolated and converted into the chloride (III, R = Cl), which on cyclisation with aluminium chloride in benzene gave an excellent yield of (IV, R = Me), identical with the methyl ether prepared from (IV, R = H).

Although we have been unable to isolate the by-product responsible for the ferric reaction given by the crude chromanone (II, R = H), it is clear that, since (IV, R = H) does not give a ferric reaction, this material must be the intermediate ketone (I, R = H). In this connexion it is of interest to note that, although the dihydro-γ-pyrone ring system of the 7-methoxy-2 : 2-dimethylchromanone (II, R = Me) undergoes scission with 5% alcoholic sodium ethoxide or with boiling 10% aqueous-alcoholic sodium hydroxide,

resulting in the formation of a product which is in all probability (I, R = Me) since it gives a strong ferric reaction, yet this ether appears to be more stable than the analogous 5 : 7-dimethoxy-2 : 2-dimethylchromanone (Part XII, *loc. cit.*) under comparable conditions. Like the latter compound, however, (II, R = Me) on treatment with semicarbazide acetate yields a *product*, $C_{13}H_{17}O_3N_3$, which is isomeric with the expected semicarbazone of (II, R = Me) but gives a strong ferric reaction and may be derived from the ketone (I, R = Me). Curiously enough, the semicarbazone obtained from 7-methoxychromanone has also been found to give a similar ferric reaction.

Attempts to reduce the coumaranone (IV, R = H) with the aid of amalgamated zinc by the method of Clemmensen gave rise to an amorphous product, whilst catalytic reduction of the diacetyl derivative (3 : 6-*diacetoxy*-2-iso*propylbenzofuran*) according to the procedure of Roll and Adams (*J. Amer. Chem. Soc.*, 1931, **53**, 3469) yielded a product which, after hydrolysis, was resolved into the coumaranone (IV, R = H) and a pleasant-smelling oil, insoluble in aqueous sodium hydroxide; the latter compound presumably arises by complete hydrogenation of the resorcinol nucleus. On the other hand, reduction of the chromanone (II, R = H) by Clemmensen's method furnished an excellent yield of the *chroman* (VI, R = H), but with hydrogen and a palladium–charcoal catalyst a product consisting of chroman, unchanged chromanone, and a small amount of alkali-insoluble material was obtained. Since in the latter procedure there is no reason to suspect that the dihydro-γ-pyrone ring opens, this result affords substantial evidence of the structure of (VI, R = H).



(V.) (VI.) (VII.) (VIII.)

The interaction of 7-benzyloxy-3 : 4-dihydrocoumarin and an excess of methylmagnesium iodide in warm benzene and decomposition of the product, presumably (V), in the usual manner gave rise to (VI, R = CH_2Ph) which on debenzylation furnished the chroman (VI, R = H), thus affording a new route to compounds of this type. Under similar conditions 7-*benzyloxy*-4-*methylcoumarin* gave rise to the *benzyloxychromen* (VII, R = CH_2Ph) (cf. Houben, *Ber.*, 1904, **37**, 498; Heilbron and Hill, J., 1927, 2005), the structure of which clearly follows from its formation by the action of methylmagnesium iodide on 7-*benzyloxy*-2 : 2-*dimethylchromanone* (II, R = CH_2Ph) and subsequent hydrolysis of the product. Catalytic hydrogenation of the *benzyl ether* (VII, R = CH_2Ph) with the aid of a palladium–charcoal catalyst was accompanied by removal of the benzyl group, and gave rise to the chroman (VIII) (isolated as the p-*nitrobenzoate*) which was identical with a specimen prepared by the hydrogenation of the *chromen* (VII, R = H) resulting from the debenzylation of (VI, R = CH_2Ph) by means of warm acetic acid containing hydrochloric acid.

In the investigations on the constitution of the chromeno-α-pyrones xanthyletin and xanthoxyletin (J., 1936, 627, 1828), it was found that degradation of the chromen system with ozone proceeded abnormally and, instead of the expected product formed by scission across the double bond in the 3 : 4-position and containing the same number of carbon atoms, an *o*-hydroxyaldehyde was obtained, in which respect the behaviour of these chromens appears to be analogous to that of a benzofuran system; *e.g.*, compare usneol (Schöpf and Heuck, *Annalen*, 1927, **459**, 233). In agreement with these results, ozonolysis of the authentic chromen (VII, R = CH_2Ph) has now been found to proceed in a similar manner, giving rise to 2-hydroxy-4-benzyloxyacetophenone.

Experimental.

7-*Hydroxy*-2 : 2-*dimethylchromanone* (II, R = H).—It was found advantageous to prepare this compound by the following modification of Arima's procedure (*loc. cit.*). Well-powdered aluminium chloride (25 g.) was gradually added to a solution of $\beta\beta$-dimethylacryl chloride (9 g.) and resorcinol (8 g.) in nitrobenzene (100 c.c.) at room temperature, and 4 days later the

mixture was treated with ice and hydrochloric acid. The product and nitrobenzene were isolated with ether, the nitrobenzene removed with steam, and the chromanone (10·5 g.) purified by crystallisation from dilute alcohol and then from chloroform–light petroleum, forming colourless needles, m. p. 172°, which gave a negative ferric reaction. This compound (7 g.) was also obtained by the interaction of resorcinol (7·5 g.), β-bromo*iso*valeryl chloride (8 g.), and aluminium chloride (22 g.) in nitrobenzene (100 c.c.) under the same conditions.

Acetylation of the chromanone (0·5 g.) with pyridine (1 c.c.) and acetic anhydride (2 c.c.) at room temperature gave the *acetate* (0·55 g.), which formed needles, m. p. 91°, from light petroleum (b. p. 60—80°) (Found: C, 66·9; H, 5·9. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%).

Prepared by the interaction of the chromanone (1 g.) with *p*-nitrobenzoyl chloride (1·2 g.) in pyridine (15 c.c.) at 60°, the p-*nitrobenzoate* (1·1 g.) separated from alcohol in elongated, straw-coloured prisms, m. p. 137° (Found: N, 4·2. $C_{18}H_{15}O_6N$ requires N, 4·1%).

Methylation of 7-hydroxy-2 : 2-dimethylchromanone (3 g.) with methyl iodide (4 c.c.) and excess of potassium carbonate in boiling acetone (120 c.c.) in the course of 5 hours gave the methyl ether (II, R = Me) (3 g.), forming rectangular plates, m. p. 77°, from light petroleum (b. p. 40—60°); like the acetate and *p*-nitrobenzoate, this is insoluble in aqueous sodium hydroxide, and has a negative ferric reaction [Found: C, 70·1; H, 6·8; OMe, 15·8. Calc. for $C_{11}H_{11}O_2(OMe)$: C, 69·9; H, 6·8; OMe, 15·0%] (cf. Arima, *loc. cit.*). Treatment of this derivative with warm alcoholic 2 : 4-dinitrophenylhydrazine hydrochloride gave the 2 : 4-*dinitrophenylhydrazone*, which separated from ethyl acetate in slender red needles, m. p. 221° (Found: N, 14·4. $C_{18}H_{18}O_6N_4$ requires N, 14·5%).

Interaction of the methyl ether and semicarbazide acetate in the usual manner gave rise to a *product* which formed elongated prisms, m. p. 226° (decomp.), from alcohol, giving a red-brown coloration with alcoholic ferric chloride (Found: C, 59·4; H, 6·6; N, 15·8. $C_{13}H_{17}O_3N_3$ requires C, 59·3; H, 6·5; N, 16·0%). By means of warm alcoholic 2 : 4-dinitrophenylhydrazine hydrochloride this compound was converted into the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 221°, after purification from ethyl acetate.

A mixture of the foregoing methyl ether (0·5 g.), veratraldehyde (0·5 g.), alcohol (4 c.c.), and 10% aqueous sodium hydroxide (3·5 c.c.) was gently refluxed for 20 minutes and diluted with water (50 c.c.). Crystallisation of the yellow precipitate, which gave a red ferric chloride reaction, from dilute alcohol finally gave a product in pale yellow plates, m. p. 80°, which had a negative ferric reaction and seemed to be the veratrylidene derivative but did not appear to be analytically pure although the m. p. remained unchanged after repeated purification (Found: C, 70·0; H, 6·5. Calc. for $C_{21}H_{22}O_5$: C, 71·2; H, 6·2%).

Acidification of the alkaline liquors left on removal of the solid gave a small amount of material having a red ferric reaction.

Attempts to prepare the veratrylidene derivative by condensation of the chromanone and veratraldehyde in acetic acid with hydrogen chloride gave rise to an amorphous product, m. p. 130—132°, after purification with the aid of alcohol. The crude material had a red ferric reaction.

On attempting to prepare the veratrylidene derivative of 7-methoxychromanone by condensation of the chromanone and veratraldehyde with boiling 10% aqueous-alcoholic sodium hydroxide, a resinous product having a strong ferric reaction was obtained, but when the reaction was carried out under the conditions employed by Pfeiffer and Grimmer (*Ber.*, 1917, **50**, 911) the required compound was obtained, m. p. 141°, identical with a specimen prepared by the hydrogen chloride–acetic acid method (Perkin, Ray, and Robinson, J., 1926, 946).

7-*Hydroxy*-2 : 2-*dimethylchroman* (VI, R = H).—(A) A mixture of 7-hydroxy-2 : 2-dimethylchromanone (2 g.), acetic acid (20 c.c.), and 18% hydrochloric acid (75 c.c.), containing amalgamated zinc dust (50 g.), was kept at room temperature for 24 hours, treated with 12% hydrochloric acid (20 c.c.), heated on the steam-bath for 1 hour, and then refluxed for 3 hours. The product was isolated with ether, and on distillation in a high vacuum gave the *chroman* (1·1 g.) as an almost colourless oil, b. p. 140—143°/0·1 mm., which slowly solidified and then separated from light petroleum (b. p. 40—60°) in colourless slender needles, m. p. 72° (Found: C, 74·2; H, 7·9. $C_{11}H_{14}O_2$ requires C, 74·2; H, 7·9%).

(B) Absorption of hydrogen by 7-hydroxy-2 : 2-dimethylchromanone (1 g.), dissolved in acetic acid (200 c.c.), containing a palladium–charcoal catalyst (from 0·2 g. of palladium chloride and 2 g. of charcoal), appeared to have ceased in about 10 hours. After the separation of the catalyst by filtration, the greater part of the acetic acid was removed in a vacuum, the residue neutralised with aqueous sodium bicarbonate, and the product isolated with ether and resolved into a small amount of an oily neutral fraction and a semi-solid phenolic fraction by means of

dilute aqueous sodium hydroxide. The latter material was extracted with boiling light petroleum, and the extract evaporated, leaving a very viscous oil from which 7-hydroxy-2 : 2-dimethylchroman was isolated by sublimation in a high vacuum (temperature of oil-bath, 110—115°), m. p. 71—72°, identical with the compound obtained by Clemmensen's method. The residue insoluble in light petroleum was found to consist of unchanged chromanone, m. p. and mixed m. p. 170—171°.

Interaction of the chroman (0·8 g.) and *p*-nitrobenzoyl chloride (1 g.) in pyridine (15 c.c.) at 60° for 6 days gave rise to the p-*nitrobenzoate* (1·2 g.), which formed colourless slender prisms, m. p. 126°, from alcohol (Found : N, 4·4. $C_{18}H_{17}O_5N$ requires N, 4·3%).

(C) In the preparation of 7-hydroxycoumarin for this work by the condensation of resorcinol and malic acid with sulphuric acid according to v. Pechmann (*Ber.*, 1884, **17**, 932), consistently poor yields were obtained. As the result of a large number of experiments in which the ratio of the reactants, the concentration of the sulphuric acid, and the temperature were varied, the following appeared to be the most satisfactory procedure :—An intimate mixture of resorcinol (3 g.), malic acid (2·46 g.), and concentrated sulphuric acid (6·1 c.c.) was heated in an oil-bath at 120° until the effervescence had ceased (about 1 hour), cooled, and treated with excess of crushed ice. The precipitated coumarin was purified by repeated crystallisation from dilute alcohol (charcoal) and obtained in pale pink prisms, m. p. 227—228° ; it was found that the crude product could be conveniently decolorised by leading a stream of sulphur dioxide into a warm concentrated alcoholic solution of the coumarin. Yield, 43% of the theoretical. Benzylation of 7-hydroxycoumarin (4 g.) was effected by means of benzyl bromide (5 c.c.) and potassium carbonate (7 g.) in boiling acetone (100 c.c.) in the course of 4—5 hours, and on isolation the *benzyl ether* separated from benzene in elongated prisms, m. p. 154° (Found : C, 76·1; H, 5·0. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%).

Hydrogenation of 7-hydroxycoumarin (3 g.), dissolved in a mixture of alcohol (10 c.c.) and 0·1*N*-aqueous sodium hydroxide (50 c.c.), containing an active palladium–charcoal catalyst, gave rise to β-2 : 4-dihydroxyphenylpropionic acid, m. p. 164—165° (decomp.), which on being kept at 130—135° for 2 hours was converted into 7-hydroxy-3 : 4-dihydrocoumarin, m. p. 132—133° after purification (cf. Späth and Klager, *Ber.*, 1933, **66**, 749; Langley and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 2320). Benzylation of this compound (4 g.) with benzyl bromide (7 c.c.) and excess of potassium carbonate in boiling acetone (50 c.c.) in the course of 4 hours gave the benzyl ether (5·8 g.) as a pale yellow oil, b. p. 220°/0·3 mm.

A solution of 7-benzyloxy-3 : 4-dihydrocoumarin (3 g.) in ether (20 c.c.) was added to methylmagnesium iodide (from 5·5 g. of methyl iodide and 0·86 g. of magnesium) in ether (25 c.c.), and the mixture refluxed for 1 hour. After isolation in the usual manner, the product was digested with dilute sodium hydroxide to remove traces of debenzylated material, and the alkali-insoluble fraction separated with ether and purified by distillation in a vacuum, giving 7-*benzyloxy*-2 : 2-*dimethylchroman* (VI, R = CH_2Ph) as an almost colourless oil (2 g.), b. p. 160—165°/0·4 mm. (Found : C, 80·6; H, 7·7. $C_{18}H_{20}O_2$ requires C, 80·6; H, 7·5%). A mixture of this compound (0·4 g.) and acetic acid (10 c.c.), containing concentrated hydrochloric acid (0·93 c.c.), was refluxed for 2 hours, diluted with water, and neutralised with sodium bicarbonate. A solution of the crude product in ether (50 c.c.) was extracted several times with 10% aqueous sodium hydroxide (5 c.c.), the combined extracts acidified with hydrochloric acid, and the resulting 7-hydroxy-2 : 2-dimethylchroman (0·11 g.) isolated with ether and purified by sublimation in a high vacuum and then by crystallisation from light petroleum (b. p. 40—60°), forming slender needles, m. p. 72°, identical with specimens prepared by methods (A) and (B) (Found : C, 74·2; H, 8·0%). Evaporation of the ethereal solution left on removal of the chroman by means of aqueous sodium hydroxide gave unchanged benzyl ether (0·17 g.).

Experiments on the debenzylation of the compound (0·5 g.) by means of hydrogen and an active palladium–charcoal catalyst gave rise to a mixture of 7-hydroxy-2 : 2-dimethylchroman and unchanged material.

3 : 6-*Diacetoxy*-2-iso*propylbenzofuran*.—6-Hydroxy-2-*iso*propyl-β-coumaranone (3 g.) (Arima and Okamoto, *J. Chem. Soc. Japan*, 1929, **50**, 344) was boiled with acetic anhydride (20 c.c.), containing sodium acetate (1·5 g.), for ½ hour, and after isolation the *diacetate* (3·5 g.) separated from light petroleum (b. p. 40—60°) in colourless elongated prisms, m. p. 56° [Found : C, 65·4; H, 5·8; Ac, 35·9. $C_{11}H_{10}O(OAc)_2$ requires C, 65·2; H, 5·8; Ac, 31·2%].

6-*Methoxy*-2-iso*propyl*-β-*coumaranone* (IV, R = Me).—(A) Methylation of 6-hydroxy-2-*iso*propyl-β-coumaranone (*loc. cit.*) (1·2 g.) with excess of methyl iodide and potassium carbonate in boiling acetone during 3 hours gave the *methyl ether*, which formed stout prisms (0·7 g.), m. p. 78°, from light petroleum (b. p. 40—60°) [Found : C, 70·0; H, 6·9; OMe, 15·3.

$C_{11}H_{11}O_2(OMe)$ requires C, 69·9; H, 6·8; OMe, 15·0%]. Mixed with the isomeric chromanone, m. p. 72°, it melted at 64—68°.

(B) The material obtained by the interaction of resorcinol monomethyl ether (12 g.) and ethyl α-bromo*iso*valerate (17 g.) in alcoholic sodium ethoxide (from 80 c.c. of alcohol and 2·1 g. of sodium) at room temperature for 14 hours and then on the water-bath for 6 hours was hydrolysed by being digested with 12% aqueous-alcoholic sodium hydroxide (60 c.c.) at 30—40°, the solution was acidified with hydrochloric acid, and the product isolated with ether and resolved by distillation in a vacuum into a little ββ-dimethylacrylic acid, resulting from the decomposition of ethyl α-bromo*iso*valerate in the course of the condensation, and *α-3-methoxyphenoxyisovaleric acid* (III, R = OH), b. p. 148—153°/·01 mm. [Found: OMe, 13·7. $C_{11}H_{13}O_3(OMe)$ requires OMe, 13·8%].

After the vigorous reaction between α-3-methoxyphenoxy*iso*valeric acid (6 g.) and phosphorus pentachloride (5·6 g.) had almost ceased, the mixture was heated at 40° for a few minutes and kept for 1 hour, and the phosphoryl chloride removed in a vacuum. To a solution of the residual acid chloride (III, R = Cl) in thiophen-free benzene (50 c.c.), maintained at 0°, powdered aluminium chloride (3·5 g.) was added in the course of ¾ hour, the reaction mixture kept at room temperature for 3 hours, and the product isolated in the usual manner and distilled in a vacuum, giving a main fraction (3·5 g.), b. p. 120—125°/0·1 mm., as a mobile oil. This material, which rapidly became dark red, was digested with 1% aqueous sodium hydroxide, and on isolation with ether the alkali-insoluble, colourless oil solidified and then separated from light petroleum (b. p. 40—60°) in colourless stout prisms, m. p. 78°, identical with the material prepared by method (A) (Found: C, 69·8; H, 6·9%). The colour which developed in the partly purified material appeared to be due to traces of an unstable alkali-soluble impurity.

Semicarbazone of 7-Methoxychromanone.—Prepared in the usual manner, this compound was found to melt at 231° (Perkin, Ray, and Robinson, J., 1926, 946, give m. p. 222°) (Found: N, 17·8. Calc. for $C_{11}H_{13}O_3N_3$: N, 17·9%). With alcoholic ferric chloride it gave a red-brown coloration.

7-Hydroxy-2 : 2 : 4-trimethyl-Δ³-chromen (VII, R = H).—(A) Benzylation of 7-hydroxy-4-methylcoumarin (Robertson and co-workers, J., 1931, 1257) (44 g.) was effected with benzyl bromide (50 c.c.) and potassium carbonate (70 g.) in boiling acetone (630 c.c.) in the course of 10 hours, and on isolation the *benzyl ether* separated from alcohol in flat rhombic prisms, m. p. 117·5° (Found: C, 76·4; H, 5·3. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%). Methylmagnesium iodide (from 5·14 g. of metal and 30 g. of methyl iodide) was prepared in ether (150 c.c.), and the solvent evaporated. A solution of 7-benzyloxy-4-methylcoumarin (19 g.) in benzene (250 c.c.) was then introduced, and the mixture refluxed for 5 hours. After isolation in the usual manner, the product was distilled in a vacuum, yielding a main fraction, b. p. 166—170°/0·25 mm., which solidified and then on repeated crystallisation from the alcohol gave *7-benzyloxy-2 : 2 : 4-trimethyl-Δ³-chromen* (VII, R = CH_2Ph) in colourless slender prisms, m. p. 58° (Found: C, 81·7; H, 7·3. $C_{19}H_{20}O_2$ requires C, 81·4; H, 7·1%). Yield, 80% of the theoretical.

A solution of the benzyl ether (3 g.) in acetic acid (75 c.c.), containing concentrated hydrochloric acid (7 c.c.), was heated on the water-bath for 1¼ hours, and the resulting green mixture poured into water (1·5 l.). Next day, the crystalline precipitate of *7-hydroxy-2 : 2 : 4-trimethyl-Δ³-chromen* was collected and purified by sublimation in a high vacuum and then by recrystallisation from light petroleum (b. p. 80—100°), forming colourless elongated prisms, m. p. 130°, soluble in alcohol or benzene (Found: C, 75·8; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

(B) *7-Benzyloxy-2 : 2-dimethylchromanone* (II, R = CH_2Ph) was prepared by benzylation of 7-hydroxy-2 : 2-dimethylchromanone (1 g.) with benzyl bromide (1·1 c.c.) and excess of potassium carbonate in boiling acetone (25 c.c.) in the course of 5 hours, and on isolation was purified by distillation in a vacuum, b. p. 172—174°/0·3 mm., and then by crystallisation from light petroleum (b. p. 80—100°), forming colourless prisms, m. p. 73° (Found: C, 76·6; H, 6·4. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%). A mixture of this compound (1 mol.), methylmagnesium iodide (1·25 mol.), and ether was refluxed for 6 hours and, after isolation in the usual manner, the product was distilled in a high vacuum. On being triturated with a little light petroleum (b. p. 40—60°), the semi-solid distillate gave a small amount of crystalline material which separated from dilute alcohol in plates, m. p. 57°, undepressed by admixture with an authentic specimen of 7-benzyloxy-2 : 2 : 4-trimethyl-Δ³-chromen, m. p. 58°. Attempts to increase the yield of this compound by varying the conditions of the reaction were entirely unsuccessful; when the Grignard reaction was carried out in toluene on the water-bath for 5 hours the product consisted mainly of a crystalline compound, m. p. 163°, which was not further investigated.

7-Hydroxy-2 : 2 : 4-trimethylchroman (VIII).—Hydrogenation of 7-benzyloxy-2 : 2 : 4-tri-

methyl-Δ^3-chromen (5 g.), dissolved in alcohol (275 c.c.), with hydrogen (950 c.c. absorbed) and a palladium–charcoal catalyst (from 2 g. of charcoal and 0·2 g. of palladium chloride) was accompanied by removal of the benzyl group, and the resulting hydroxy-chroman was obtained as a very viscous, almost colourless liquid, insoluble in water and having a negative ferric reaction, which has not been crystallised. On treatment with an excess of *p*-nitrobenzoyl chloride dissolved in pyridine at room temperature for several days and then at 60—65° for 3 hours, this material gave an almost theoretical yield of the p-*nitrobenzoate*, which separated from alcohol in pale straw-coloured, slender needles, m. p. 137° (Found: C, 67·0; H, 5·7. $C_{19}H_{19}O_5N$ requires C, 66·9; H, 5·6%). 8% Aqueous sodium hydroxide (20 c.c.) was added to a solution of this ester (3·5 g.) in hot alcohol (40 c.c.), and the mixture kept for ½ hour. On isolation, the recovered hydroxychroman was obtained as a very viscous liquid which, after being purified by distillation in a high vacuum, did not solidify.

On hydrogenation of 7-hydroxy-2 : 2 : 4-trimethyl-Δ^3-chromen (0·75 g.), dissolved in alcohol (100 c.c.), with the aid of a platinum catalyst (0·1 g.), the chroman was obtained as a viscous liquid, which was characterised by formation of the *p*-nitrobenzoate, m. p. and mixed m. p. 137°, after crystallisation from alcohol.

Ozonolysis of 7-Benzyloxy-2 : 2 : 4-trimethyl-Δ^3*-chromen.*—A stream of ozone and oxygen (rate approx. 50—60 c.c./min.) was led into a solution of the chromen (2 g.) in chloroform (75 c.c.) for 1½ hours, the solvent removed, and the residue hydrolysed with water. Distillation of the product in a high vacuum gave a solid, m. p. about 94°, which on crystallisation from alcohol yielded 2-hydroxy-4-benzyloxyacetophenone, m. p. 105°, identified by comparison with an authentic specimen, m. p. 105—106°, prepared by partial benzylation of resacetophenone (E.P. 377464; *Centr.*, 1932, **2**, 2485, gives m. p. 105—106° but Venkataraman and co-workers, J., 1934, 1766, give m. p. 111°).

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