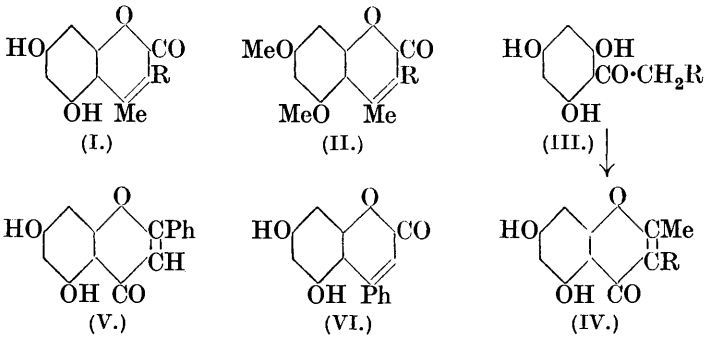
CLXVI.—*Hydroxy-carbonyl Compounds. Part III. The Preparation of Coumarins and* 1 : 4-*Benzopyrones from Phloroglucinol and Resorcinol.*

By FREDERICK W. CANTER, FRANK H. CURD, and ALEXANDER ROBERTSON.

ACCORDING to the well-known method of Pechmann esters of acylacetic acids condense with phenols in the presence of sulphuric acid (or zinc chloride) to give coumarins. Though Jacobson and Ghosh (J., 1915, **107**, 424, 1051) concluded that in certain instances the products obtained by this reaction were 1 : 4-benzopyrones, it has been shown conclusively that the compounds to which these authors have ascribed a 1 : 4-pyrone structure are coumarins (Baker and Robinson, J., 1925, **127**, 1981; Baker, *ibid.*, p. 2349). On the other hand, when phosphoric oxide replaces sulphuric acid as the condensing agent, Simonis and his co-workers (*Ber.*, 1913, **46**, 2014; 1914, **47**, 697, 2229) have found that the reaction takes the alternative course and 1 : 4-pyrones are formed. Accordingly, therefore, the procedure of Simonis seemed to us to offer a convenient solution of the problem of independently synthesising the 1 : 4-benzopyrones (IV, R = Me) and (IV, R = Et) which we consider to be formed by ring closure of the ketones (III, R = Me) and (III, R = Et) by means of sodium acetate and acetic anhydride. Further, by

methylating the products we hoped to obtain the dimethyl ethers of (IV, R = Me) and (IV, R = Et) described in the previous paper.

The condensation of phloroglucinol and ethyl α-methylacetoacetate under the influence of phosphoric oxide proceeded readily, but in place of the expected 1 : 4-pyrone (IV, R = Me) it resulted in the formation of the *coumarin* (I, R = Me). This substance was identical with a specimen prepared by the method of Pechmann.

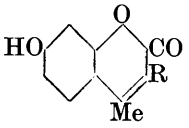


Further, the interaction of phloroglucinol dimethyl ether and the same ester in the presence of phosphoric oxide afforded the *dimethyl* ether (II, R = Me) identical with the ether derived from an authentic specimen of the coumarin (I, R = Me). In a similar manner the condensation of phloroglucinol and the appropriate esters gave rise to the coumarins (I, R = H) (Pechmann and Cohen, *Ber.*, 1884, **17**, 2189) and (I, R = Et). Identical specimens of the *ether* (II, R = H) were obtained from phloroglucinol dimethyl ether by the procedure of Simonis and by methylating Pechmann and Cohen's product. Attempts to use sulphuric acid as the condensing agent in the direct preparation of the dimethyl ethers led to the formation of products which appeared to be partially demethylated.

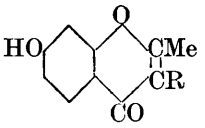
Although Simonis and Remmert (*Ber.*, 1914, **47**, 2229) obtained flavone in small yield by condensing phenol and the sodium derivative of ethyl benzoylacetate, on the basis of the foregoing results it appeared unlikely that phloroglucinol would give rise to chrysin (V) (Robinson and Venkataraman, J., 1926, 2344). Instead a good yield of the coumarin (VI) (Kostanecki and Weber, *Ber.*, 1893, **26**, 2906) results from the condensation of phloroglucinol and ethyl benzoylacetate with the aid of phosphoric oxide. The production of (VI) from phlorbenzophenone by ring closure with sodium acetate and acetic anhydride places the constitution of this compound beyond doubt.

In view of the unexpected behaviour of phloroglucinol we extended our investigation to resorcinol. The condensation of this phenol

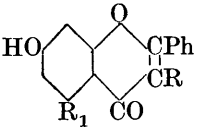
and ethyl α-methylacetoacetate has been described by Simonis and Remmert (*loc. cit.*) (compare Heilbron and co-workers, J., 1923, **123**, 2559), who assumed that the product was 7-hydroxy-2 : 3-dimethyl-1 : 4-benzopyrone (Kostanecki and Lloyd, *Ber.*, 1901, **34**, 2942). On repeating the experiment, we found that the product was identical with a specimen of 7-hydroxy-3 : 4-dimethylcoumarin (VII, R = Me) (Pechmann and Duisberg, *Ber.*, 1883, **16**, 2119). Careful comparison of the respective *acetyl* derivatives and methyl and ethyl ethers failed to show any divergence. Kostanecki and Lloyd (*loc. cit.*) have synthesised the isomeric 1 : 4-pyrone (VIII, R = Me) by a method which leaves no doubt as to its constitution.



(VII.)



(VIII.)



(IX.)

These authors obtained the same pyrone from respropiophenone by ring closure with acetic anhydride and sodium acetate. We have found that Kostanecki and Lloyd's 1 : 4-pyrone is not identical with either Pechmann and Duisberg's coumarin or with Simonis and Remmert's compound. The same lack of identity was revealed on comparing the respective acetyl derivatives and ethers (methyl and ethyl). Similarly, resorcinol and ethyl acetoacetate furnished the coumarin (VII, R = H) (Pechmann and Duisberg, *loc. cit.*). The condensation of ethyl α-ethylacetoacetate and resorcinol by means of either sulphuric acid or phosphoric oxide gave the *coumarin* (VII, R = Et). By analogy with respropiophenone the product obtained by the vigorous acetylation of resbutyrophenone is the 1 : 4-*pyrone* (VIII, R = Et).

In order to effect the condensation of certain monohydric phenols with acylacetates unsubstituted in the α-position Simonis and his collaborators found it essential to use the sodium derivative of the ester. In our experiments with resorcinol and phloroglucinol it has been found unnecessary to use the sodium compounds.

The preparation of the 3-alkylflavones (IX, R = Me; R_1 = H), (IX, R = Me; R_1 = OH), and (IX, R = Et; R_1 = OH) by Robinson's method is described. Vigorous acetylation of phloracetophenone gave rise to two products both of which appear to contain nuclear acetyl groups (compare Shinoda, *J. Pharm. Soc. Japan*, 1928, **48**, 35).

EXPERIMENTAL.

5 : 7-*Dihydroxy*-4-*methylcoumarin* (I, R = H).—Phosphoric oxide (5 g.) was added with stirring to a mixture of phloroglucinol (2 g.)

and ethyl acetoacetate (2 g.), and the vigorous reaction moderated by occasional cooling in tap-water. When the reaction had ceased, the solid mixture was ground under water and the product was collected and washed with much water. Crystallised from acetic acid, the coumarin separated as a hydrate in flat prisms, m. p. 292—293° (Found : C, 57·4; H, 5·2. Calc. for $C_{10}H_8O_4,H_2O$: C, 57·2; H, 4·8%). The diacetate crystallised from alcohol in needles, m. p. 150—151°.

A specimen of this coumarin prepared according to the directions of Pechmann and Cohen (*loc. cit.*) had m. p. 292°, alone or mixed with the product prepared by the phosphoric acid method; the diacetate had m. p. and mixed m. p. 150—151° (Pechmann and Cohen give the m. p.'s of the coumarin and its diacetate as 282—284° and 138—140° respectively). In another experiment using sulphuric acid, we found that the coumarin had m. p. 282—284° after one crystallisation from acetic acid. Repeated purification gave a product, m. p. 285—286°, which, mixed with a specimen prepared by the Simonis reaction, melted at 287—288°. The diacetate of this product, m. p. 285—286°, had m. p. and mixed m. p. 150—151°.

5 : 7-*Dimethoxy*-4-*methylcoumarin* (II, R = H).—(A) Methylation of Pechmann and Cohen's coumarin (2·7 g.) was effected by means of methyl iodide (16 c.c.) and potassium carbonate (10 g.) in boiling acetone (40 c.c.) during 48 hours. Crystallised from acetic acid and then from methyl alcohol, the *dimethyl* ether formed colourless needles, m. p. 171° [Found : C, 65·3; H, 5·8; OMe, 27·8. $C_{10}H_6O_2(OMe)_2$ requires C, 65·5; H, 5·4; OMe, 28·2%]. It is moderately easily soluble in alcohol or warm acetone. An alcoholic solution exhibits a blue fluorescence. The coumarin dissolves in concentrated sulphuric acid to a pale straw-coloured solution exhibiting a bluish-green fluorescence.

(B) The vigorous interaction between phloroglucinol dimethyl ether (2·3 g.) and ethyl acetoacetate (2 g.) in the presence of phosphoric oxide (5 g.) was moderated by cooling in tap-water. After the reaction had ceased, excess of water was added, and the solid collected and washed with water. 5 : 7-Dimethoxy-4-methylcoumarin crystallised from methyl alcohol in needles, m. p. and mixed m. p. 171° (Found : C, 65·9; H, 5·6%). Yield, 70% of the theoretical.

Acetylation of Phloracetophenone.—A mixture of the ketone (5 g.), sodium acetate (5 g.), and acetic anhydride (30 c.c.) was heated at 170—180° for 12 hours, and the product isolated in the usual manner. The solid was dissolved in warm alcohol and, on cooling, the main portion (X) (3·6 g.) separated. Repeated crystallisation from dilute

alcohol finally gave (X) in colourless needles, m. p. 127° (Found: C, 60·8; H, 4·7. $C_{16}H_{14}O_7$ requires C, 60·4; H, 4·4%). Removal of the acetyl groups by means of cold 4% methyl-alcoholic potassium hydroxide gave a *compound* which crystallised from alcohol in needles, m. p. 226° (Found: C, 61·3; H, 4·6. $C_{12}H_{10}O_5$ requires C, 61·5; H, 4·3%). With alcoholic ferric chloride this substance gives a red coloration.

After the crude compound (X) had been removed, the alcoholic mother-liquor on standing deposited an isomeric substance (Y), which crystallised from alcohol in almost colourless plates, m. p. 131° (Found: C, 60·9; H, 4·6%). A mixture of (X) and (Y) melted at 107—108°. On hydrolysis, Y yielded a product which separated from dilute alcohol in elongated prisms, m. p. 274° after sintering at 269° (Found: C, 61·6; H, 4·5%). With alcoholic ferric chloride it gives a brown coloration. A mixture of the two deacetylated products melted at about 214°.

5 : 7-*Dihydroxy*-3 : 4-*dimethylcoumarin* (I, R = Me).—(A) A mixture of phloroglucinol (5·6 g.), ethyl α-methylacetoacetate (6·4 g.), and 75% sulphuric acid (30 c.c.) was heated on the steam-bath for ½ hour. Addition of water (300 c.c.) to the cooled reaction mixture precipitated the *coumarin* as a yellow solid. Recrystallised from acetic acid and then from methyl alcohol, it formed colourless needles, m. p. 291—292° (Found in material dried at 110°: C, 64·1; H, 5·3. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%). The substance is readily soluble in hot alcohol or acetic acid and does not give a ferric chloride reaction. It dissolves in concentrated sulphuric acid to a colourless solution which exhibits a blue fluorescence. The *diacetate* separates from warm alcohol in elongated prisms, m. p. 130° (Found: C, 62·1; H, 5·0. $C_{15}H_{14}O_6$ requires C, 62·1; H, 4·8%).

(B) When phloroglucinol (2·5 g.), ethyl α-methylacetoacetate (2 g.), and phosphoric oxide (5 g.) were mixed, a vigorous reaction ensued. After ½ hour the mixture was heated on the steam-bath for 15 minutes. After isolation, the coumarin crystallised from methyl alcohol in colourless needles, m. p. and mixed m. p. 291—292° (Found in material dried at 110°: C, 64·3; H, 5·0%). The diacetate formed elongated prisms, m. p. and mixed m. p. 130°.

5 : 7-*Dimethoxy*-3 : 4-*dimethylcoumarin* (II, R = Me).—(A) A mixture of phloroglucinol dimethyl ether (2·2 g.), ethyl α-methylacetoacetate (2·2 g.), and phosphoric oxide (5 g.) reacted vigorously when warmed. After ½ hour, excess of water was added, and the product collected. Crystallised from acetic acid and then from methyl alcohol, the *substance* formed colourless silky needles, m. p. 157—158° (Found: C, 66·1; H, 5·8. $C_{13}H_{14}O_4$ requires C, 66·6; H, 6·0%). It is readily soluble in warm alcohol or acetone or ethyl acetate and

sparingly soluble in ether. An alcoholic solution of the coumarin exhibits a faint blue fluorescence. It dissolves in concentrated sulphuric acid to a pale straw-coloured solution exhibiting a blue-violet fluorescence.

(B) A specimen of 5 : 7-dihydroxy-3 : 4-dimethylcoumarin prepared by Pechmann's method was methylated by means of methyl iodide and potassium carbonate in boiling acetone. The dimethyl ether crystallised from methyl alcohol in silky needles, m. p. and mixed m. p. 157—158° [Found : C, 66·6; H, 6·0; MeO, 26·0. Calc. for $C_{11}H_8O_2(OMe)_2$: C, 66·6; H, 6·0; OMe, 26·5%].

5 : 7-*Dihydroxy*-2 : 3-*dimethyl*-1 : 4-*benzopyrone* (IV, R = Me).—Vigorous acetylation of phlorpropiophenone (3 g.) by means of sodium acetate (3 g.) and acetic anhydride (20 c.c.) at 170—180° during 12 hours gave the *diacetate* of the pyrone (4·5 g.), which crystallised from alcohol in colourless needles, m. p. 141—142° (Found : C, 61·9; H, 5·1. $C_{15}H_{14}O_6$ requires C, 62·1; H, 4·8%). Deacetylation was effected by boiling 10% aqueous sodium carbonate, and, on isolation, the *pyrone* separated from alcohol as a hydrate in colourless slender needles, m. p. 215° (Found in material dried at 130° : C, 64·3; H, 5·1. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%). It is readily soluble in cold ethyl acetate and in warm alcohol. Addition of a drop of ferric chloride to an alcoholic solution gives a deep red-violet coloration.

5 : 7-*Dihydroxy*-3-*methylflavone* (IX, R = Me; R_1 = OH).—Benzoic anhydride (18 g.), sodium benzoate (4 g.), and phlorpropiophenone (3 g.) were ground together and heated for 12 hours in an oil-bath at 180—190°. The product was dissolved in boiling 80% alcohol (90 c.c.), a solution of potassium hydroxide (20 g.) in water (20 c.c.) gradually added, the mixture boiled for 20 minutes, water (250 c.c.) added, and the *flavone* precipitated with carbon dioxide. Crystallised from methyl alcohol, it formed tufts of pale straw-coloured needles, m. p. 262° (Found : C, 71·6; H, 4·9. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%). The substance is moderately easily soluble in warm alcohol and acetic acid. With alcoholic ferric chloride it gives a brown-violet coloration. The *diacetate* separates from alcohol in almost colourless needles, m. p. 132° (Found : C, 68·3; H, 4·9. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·5%).

5 : 7-*Dihydroxy*-4-*methyl*-3-*ethylcoumarin* (I, R = Et).—(A) 73% Sulphuric acid (35 c.c.) was slowly added to a mixture of phloroglucinol (5 g.) and ethyl α-ethylacetoacetate (6·3 g.), and the solution heated on the steam-bath until it became turbid. The cooled reaction mixture was kept at room temperature for 1 hour and poured into ice-water. The *coumarin* obtained crystallised from dilute alcohol in pale yellow, tiny, rhombic prisms (4 g.), m. p. 217°

(Found in dried material: C, 65·2; H, 5·8. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%). It dissolves in concentrated sulphuric acid to a colourless solution which exhibits a blue fluorescence. The *diacetate* separated from dilute alcohol in colourless needles, m. p. 124° (Found: C, 63·6; H, 5·6. $C_{16}H_{16}O_6$ requires C, 63·2; H, 5·3%).

Methylation of the coumarin (2 g.) by means of methyl iodide (10 c.c.) and potassium carbonate (6 g.) in boiling acetone (50 c.c.) during 6 hours afforded the *dimethyl* ether, which crystallised from dilute alcohol in pale yellow needles (1·7 g.), m. p. 112° (Found: C, 67·5; H, 6·6. $C_{14}H_{16}O_4$ requires C, 67·7; H, 6·5%). The colourless solution of the compound in concentrated sulphuric acid exhibits a blue-green fluorescence.

(B) Phosphoric oxide was gradually added to a mixture of phloroglucinol (5 g.) and ethyl α-ethylacetoacetate (6·3 g.) until a stiff paste was formed; the vigorous reaction which followed the addition of each portion of oxide was allowed to subside before a further quantity was added. The mass was thoroughly extracted with water, and the yellow powder collected and crystallised from 50% alcohol. The coumarin formed pale yellow, rhombic prisms (4 g.), m. p. and mixed m. p. 217° (Found: C, 65·3; H, 5·7%). The diacetyl derivative and the dimethyl ether were identical with the corresponding derivatives described above and melted at 124° and 112° respectively.

5 : 7-*Dihydroxy*-2-*methyl*-3-*ethyl*-1 : 4-*benzopyrone* (IV, R = Et).—Acetylation of phlorbutyrophenone (5 g.) with sodium acetate (10 g.) and acetic anhydride (25 c.c.) at 170—180° during 12 hours gave rise to the *diacetyl* derivative of the pyrone. It crystallised from alcohol (charcoal) in elongated rectangular prisms (4 g.), m. p. 124° (Found: C, 62·9; H, 5·4. $C_{16}H_{16}O_6$ requires C, 63·2; H, 5·3%). Hydrolysis of the diacetate (2·7 g.) was effected by means of warm 10% sodium hydroxide solution, and, on isolation, the *pyrone* separated from 50% alcohol (charcoal) in colourless needles, m. p. 206—207° (Found: C, 65·7; H, 5·7. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%). It forms a colourless solution in concentrated sulphuric acid which exhibits a faint blue fluorescence.

5 : 7-*Dihydroxy*-3-*ethylflavone* (IX, R = Et; R_1 = OH).—An intimate mixture of phlorbutyrophenone (3 g.), benzoic anhydride (18 g.), and sodium benzoate (10 g.) was heated at 180—185° (oil-bath) for 10 hours. The cooled melt was powdered and dissolved in alcohol (100 c.c.). A solution of potassium hydroxide (10 g.) in water (20 c.c.) was introduced and after ½ hour's refluxing the greater part of the alcohol was evaporated, the residue dissolved in water, and the *flavone* precipitated by saturating the liquid with carbon dioxide. Crystallised from alcohol, it formed almost colourless,

elongated prisms, m. p. 243° (Found : C, 72·5; H, 5·1. $C_{17}H_{14}O_4$ requires C, 72·4; H, 5·0%).

5 : 7-*Dihydroxy*-4-*phenylcoumarin* (VI).—(A) Phlorbenzophenone (5 g.) was acetylated with sodium acetate (5 g.) and acetic anhydride (30 c.c.) at 170—180° during 12 hours. On isolation, the diacetate of the coumarin crystallised from acetic acid in rectangular prisms and from alcohol in needles, m. p. 183° (Found : C, 67·3; H, 4·5. Calc. for $C_{19}H_{14}O_6$: C, 67·4; H, 4·1%) (Kostanecki and Weber, *loc. cit.*, give m. p. 181°). Deacetylation of this derivative by means of cold 4·5% potassium hydroxide solution afforded the coumarin, which crystallised from dilute alcohol in needles, m. p. 235—236° (Found : C, 70·8; H, 4·3. Calc. for $C_{15}H_{10}O_4$: C, 70·9; H, 3·8%).

A specimen of this coumarin prepared by the method of Kostanecki and Weber had m. p. and mixed m. p. 235—236°.

(B) A mixture of phloroglucinol (2·5 g.), ethyl benzoylacetate (3·3 g.), and phosphoric oxide (7 g.) was heated on the steam-bath for 2 hours and cooled, water (50 c.c.) added, and the solid collected. Crystallised from acetic acid and then from dilute methyl alcohol, the coumarin formed colourless needles, m. p. 235—236° (Found : C, 70·5; H, 3·8%). Mixed with an authentic specimen, it showed no depression of the melting point.

7-*Hydroxy*-4-*methylcoumarin* (VII, R = H).—The condensation of resorcinol (5 g.) and ethyl acetoacetate (6 g.) was effected by excess of phosphoric oxide. The resulting stiff paste was extracted with water, and the insoluble product collected and crystallised from dilute alcohol. 7-Hydroxy-4-methylcoumarin formed clusters of colourless needles (5 g.), m. p. 185—186° (Found : C, 68·3; H, 5·0. Calc. for $C_{10}H_8O_3$: C, 68·2; H, 4·6%). An authentic specimen of the coumarin was prepared by the method of Pechmann and Duisberg (*loc. cit.*) (the use of 73% sulphuric acid in place of concentrated acid gave an improved yield) and a mixture of the two products melted at 185—186°. Both specimens gave the same acetyl derivative, m. p. 150°, and the same methyl ether, m. p. 159°.

7-*Hydroxy*-2 : 3-*dimethyl*-1 : 4-*benzopyrone* (VIII, R = Me).—Respropiophenone was prepared by the application of the method of Hoesch. Resorcinol (10 g.) and propionitrile (7·5 g.) were condensed in dry ether by means of hydrogen chloride in the presence of zinc chloride, and the resulting ketimine hydrolysed by boiling with water (100 c.c.) for ½ hour. On cooling, the ketone (7 g.) crystallised, hydrate, m. p. 57°; anhydrous compound, m. p. 101·5° (Found in dried material : C, 65·1; H, 6·4. Calc. for $C_9H_{10}O_3$: C, 65·1; H, 6·1%) (Hantzsch, *Ber.*, 1906, **39**, 3094, gives m. p. of anhydrous ketone 97·5°).

Acetylation of respropiophenone (8 g.) with sodium acetate (8 g.)

and acetic anhydride (50 c.c.) at 170—180° afforded the acetyl derivative of the pyrone (6 g.), m. p. 116° (Found: C, 67·3; H, 5·2. Calc. for $C_{13}H_{12}O_4$: C, 67·2; H, 5·2%) (compare Kostanecki and Lloyd, *Ber.*, 1901, **34**, 2948). Removal of the acetyl group by means of warm 2·5% potassium hydroxide solution gave 7-hydroxy-2 : 3-dimethyl-1 : 4-benzopyrone, slender rhombic prisms, m. p. 265° (Found: C, 69·6; H, 5·5. Calc. for $C_{11}H_{10}O_3$: C, 69·5; H, 5·3%) (Wittig, *loc. cit.*, gives m. p. 257—258°; Kostanecki and Lloyd, m. p. 262°). The methyl ether, m. p. 127° (Found: C, 70·3; H, 6·0. Calc. for $C_{12}H_{12}O_3$: C, 70·6; H, 5·9%), and the ethyl ether, m. p. 124° (Found: C, 71·6; H, 6·5. Calc. for $C_{13}H_{14}O_3$: C, 71·5; H, 6·4%), were prepared by the potassium carbonate–acetone method and were identical with the ethers described by Kostanecki and Lloyd.

7-*Hydroxy*-3 : 4-*dimethylcoumarin* (VII, R = Me).—The condensation of resorcinol and ethyl α-methylacetoacetate has been repeated according to the directions of Simonis and Remmert (*loc. cit.*) and the product obtained in colourless rectangular prisms, m. p. 258°, unchanged by repeated crystallisation. An authentic specimen of the coumarin (Pechmann and Duisberg, *loc. cit.*) had m. p. 258° (these authors record m. p. 256°). A mixture of the two products had the same melting point, but a mixture of either product with 7-hydroxy-2 : 3-dimethyl-1 : 4-benzopyrone showed a depression of about 40°.

The *acetyl* derivative crystallised from alcohol in slender curved needles, m. p. 164°, and was identical with a specimen prepared from Pechmann and Duisberg's coumarin (Found: C, 67·2; H, 5·4. $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2%). Mixed with 7-acetoxy-2 : 3-dimethyl-1 : 4-benzopyrone, it melted at 104—108°.

Methylation by the potassium carbonate–acetone method afforded the methyl ether, m. p. 142·5° [Found: C, 70·9; H, 6·2; OMe, 14·8. Calc. for $C_{11}H_9O_2(OMe)$: C, 70·6; H, 5·9; OMe, 15·2%] (Heilbron, Barnes, and Morton, *loc. cit.*, give m. p. 140°). This compound was identical with the ether derived from an authentic specimen of the coumarin. Mixed with 7-methoxy-2 : 3-dimethyl-1 : 4-benzopyrone, it showed a depression in the melting point of about 38°.

The ethyl ether was prepared in a similar way, m. p. 120°, unchanged in admixture with a specimen prepared from Pechmann and Duisberg's coumarin [Found: C, 71·3; H, 6·1; OEt, 20·6. Calc. for $C_{11}H_9O_2(OEt)$: C, 71·5; H, 6·4; OEt, 20·6%] (Heilbron, Barnes, and Morton record m. p. 124°). Mixed with a specimen of 7-ethoxy-2 : 3-dimethyl-1 : 4-benzopyrone, it melted at 93—98°. It forms a colourless solution in concentrated sulphuric acid showing a violet-blue fluorescence.

7-*Hydroxy*-3-*methylflavone* (IX, R = Me; R_1 = H).—An intimate mixture of respropiophenone (3 g.), benzoic anhydride (16 g.), and sodium benzoate (6 g.) was heated at 180—185° (oil-bath) for 10 hours. The cooled melt was dissolved in warm alcohol (150 c.c.), and potassium hydroxide (10 g.) in water (20 c.c.) gradually introduced. After ½ hour's refluxing the greater part of the alcohol was distilled and the residue dissolved in warm water. The *flavone* was precipitated with carbon dioxide and crystallised from ethyl alcohol (charcoal), forming slender needles (2·5 g.), m. p. 278° (Found: C, 76·1; H, 4·8. $C_{16}H_{14}O_3$ requires C, 76·2; H, 4·8%). The *acetate* separated from alcohol in needles, m. p. 137° (Found: C, 73·3; H, 4·8. $C_{18}H_{16}O_4$ requires C, 73·5; H, 4·8%).

7-*Hydroxy*-2-*methyl*-3-*ethyl*-1 : 4-*benzopyrone* (VIII, R = Et).—A mixture of resbutyrophenone (Karrer and Rosenfeld, *Helv. Chim. Acta*, 1921, **4**, 707) (4 g.), sodium acetate (7 g.), and acetic anhydride (20 c.c.) was heated at 170—180° for 10 hours. After isolation, the oily product was dissolved in warm 10% potassium hydroxide solution, and after 1 hour the mixture was acidified. The *pyrone* thus precipitated crystallised from ethyl alcohol in prismatic needles (2 g.), m. p. 238° (Found: C, 70·6; H, 5·9. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%). It forms a colourless solution in concentrated sulphuric acid which exhibits a faint blue fluorescence.

7-*Hydroxy*-4-*methyl*-3-*ethylcoumarin* (VII, R = Et).—(A) 73% Sulphuric acid (35 c.c.) was carefully added to a mixture of resorcinol (5 g.) and ethyl α-ethylacetoacetate (7·3 g.), and the reaction completed by heating on the steam-bath for 20 minutes. On cooling, the reaction mixture was poured on ice, and the solid collected. The *coumarin* separated from dilute alcohol in tiny, colourless, rectangular prisms (5 g.), m. p. 196° (Found: C, 70·3; H, 5·9. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%). The *acetyl* derivative crystallised from dilute alcohol in irregular hexagonal plates, m. p. 107° (Found: C, 68·3; H, 6·0. $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7%). Methylation by the methyl iodide–acetone method afforded the *methyl* ether, which formed needles, m. p. 93°, from alcohol (Found: C, 71·9; H, 6·6. $C_{13}H_{14}O_3$ requires C, 71·6; H, 6·4%). The colourless solution of this derivative in concentrated sulphuric acid exhibits an intense blue fluorescence.

(B) Resorcinol (5 g.) and ethyl α-ethylacetoacetate (7·3 g.) were condensed by the gradual addition of excess of phosphoric oxide; the reaction was completed by heating at 50° for ½ hour. On isolation, the coumarin (4 g.) crystallised from alcohol (charcoal) in tiny rectangular prisms (4 g.), m. p. 198° (Found: C, 70·3; H, 6·2%). Mixed with a specimen prepared by method (A), it melted at 196—198° [A mixture of either specimen with the isomeric pyrone

(VIII, R = Et) showed a depression of about 28°]. The acetyl derivative had m. p. and mixed m. p. 107°, and the methyl ether, m. p. and mixed m. p. 93°.

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