440. *Furano-compounds. Part X. α-Acylcoumarones and a New Synthesis of 6-Hydroxy-2-*iso*propylcoumaran.*

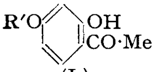
By J. B. D. Mackenzie, Alexander Robertson, and (in part) Anis Bushra and R. Towers.

The application of the Hoesch reaction to 6-hydroxy-3-methylcoumarone with methyl, phenyl, and *p*-methoxyphenyl cyanide has been shown to give 6-hydroxy-2-acyl-3-methylcoumarones, type (III), the orientations of which have been confirmed by independent syntheses.

Interaction of ethyl 6-benzyloxycoumarone-2-carboxylate and methylmagnesium iodide gave rise to 6-benzyloxy-2-(1-hydroxy*iso*propyl)coumarone (IX) whilst with an excess of the latter reagent 6-benzyloxy-2-acetylcoumarone furnished 6-benzyloxy-2-*iso*propenylcoumarone (X) which on simultaneous hydrogenation and debenzylation yielded 6-hydroxy-2-*iso*propylcoumaran (XI; R′ = R″ = H). Prepared in a similar manner 6-methoxy-3-methyl-2-*iso*propenylcoumarone formed an adduct with maleic anhydride and on hydrogenation gave 6-methoxy-3-methyl-2-*iso*propylcoumaran (XI; R′ = R″ = Me).

By analogy with the established behaviour of 3-methyl- and hydroxy-3-methyl-coumarones, type (IV) (*J.*, 1938, 306; 1939, 92, 1594; 1948, 2254), in invariably forming α-formyl derivatives in the Gattermann aldehyde synthesis it appeared likely that the application of the Hoesch reaction to these coumarones would result in the formation of the α-acyl derivatives, type (III, R″ = Alkyl or Aryl). It therefore, seemed of interest to examine the products of the latter reaction more especially in view of the claims of Karrer *et al.* (*Helv. Chim. Acta*, 1919, **2**, 454; 1921, **4**, 718) to have prepared 5-acyl derivatives, type (V), by the condensation of 6-

hydroxy-3-methylcoumarone with phenyl and *p*-methoxyphenyl cyanide. To the ketones, type (V), the Swiss workers have applied the name depsenone.



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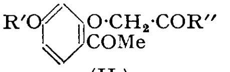

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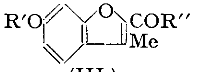

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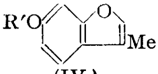

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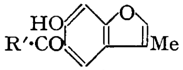

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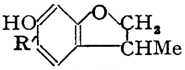

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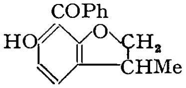
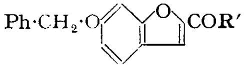


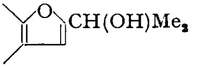
(VII.)

The condensation of methyl cyanide with 6-hydroxy-3-methylcoumarone (IV; R′ = H) by Hoesch's method gave only one product, 6-*hydroxy*-2-*acetyl*-3-*methylcoumarone* (III; R′ = H, R″ = Me) which did not give a ferric reaction in alcohol and on methylation furnished 6-*methoxy*-2-*acetyl*-3-*methylcoumarone* (III; R′ = R″ = Me), identical with the ketone obtained when (IV; R′ = H) was replaced by (IV; R′ = Me) in the Hoesch reaction and when acetyl chloride was allowed to react with (IV; R′ = Me) according to the Friedel–Crafts method with stannic chloride as the condensing agent. The failure of the Hoesch reaction product from (IV; R′ = H) to give a ferric reaction clearly excluded the possibility of the compound being an *o*-hydroxy-ketone, type (V; R′ = Me). The orientation now alloted to the Hoesch product (III; R′ = H, R″ = Me) was confirmed by an independent synthesis of the ether (III; R′ = R″ = Me), *viz.* the interaction of (I; R′ = Me) with chloroacetone in boiling acetone containing potassium carbonate which was accompanied by the cyclisation of the initial reaction product (II; R′ = R″ = Me), giving rise to 6-methoxy-2-acetyl-3-methylcoumarone (III; R′ = R″ = Me) identical with the product prepared directly from (IV; R′ = Me). By the same procedure it has been shown that the condensation product, m. p. 159°, from phenyl cyanide and 6-hydroxy-3-methylcoumarone is 6-*hydroxy*-2-*benzoyl*-3-*methylcoumarone* (III; R′ = H, R″ = Ph) and not 6-hydroxy-5-benzoyl-3-methylcoumarone (V; R′ = Ph) as claimed by Karrer *et al.* (*loc. cit.*). The benzyl ether of the Hoesch reaction product was identical with a specimen synthesised by the interaction of (I; R′ = Ph·CH$_2$) and ω-bromoacetophenone in boiling acetone containing potassium carbonate with simultaneous cyclisation of the intermediate (II; R′ = Ph·CH$_2$, R″ = Ph). Debenzylation of the ether prepared by the latter route gave (III; R′ = H, R″ = Ph) identical with the compound prepared by Hoesch's method. The corresponding *methyl ether* has the formula (III; R′ = Me, R″ = Ph). Attempts to condense phenyl cyanide with 6-hydroxy-3-methylcoumaran (VI; R′ = H) by the Hoesch method gave negative results but the interaction of the coumaran with benzoyl chloride according to the Friedel–Crafts procedure gave rise to a ketone, m. p. 172°, which has an intense red ferric reaction in alcohol and is either 6-hydroxy-5-benzoyl- (VI; R′ = Ph·CO) or 6-hydroxy-7-benzoyl-3-methylcoumaran (VII). With regard to the orientation of this compound, m. p. 172°, it may be noted that Kostanecki *et al.* (*Ber.*, 1907, **40**, 3660; 1908, **41**, 1327, 1330) concluded on general grounds that the condensation of coumaran and of 6-methoxy-3-methylcoumaran with aroyl chlorides gave products, type (VI; R′ = Ph·CO), but the absolute orientation of their compounds was not undertaken. We therefore, provisionally assign structure (VI; R′ = Ph·CO) to the *o*-hydroxybenzoyl-3-methylcoumaran obtained from (VI; R′ = H). In view of the fact that the application of the Fries reaction to 6-acetoxy-2-*iso*propylcoumaran gave 6-hydroxy-7-acetyl-2-*iso*propylcoumaran (Part V, *J.*, 1939, 933) we do not regard the orientation (VII) for the benzoylcoumaran as being entirely excluded. Karrer *et al.* (*loc. cit.*) claimed to have prepared 6-hydroxy-5-benzoyl-3-methylcoumaran, m. p. 159°, from 6-hydroxy-3-methylcoumaran and phenyl cyanide by Hoesch's method but, since it would appear that their starting material was mainly 6-hydroxy-3-methylcoumarone (IV; R′ = H) (Part VIII, *loc. cit.*), it seems likely that the substance stated to melt at 159° was in fact mainly, if not entirely, 6-hydroxy-2-benzoyl-3-methylcoumarone, which we have found to melt at 158°.

In agreement with the foregoing results it has also been shown that when phenyl cyanide is replaced by *p*-methoxyphenyl cyanide in the Hoesch reaction applied to 6-hydroxy-3-methylcoumarone the product is 6-*hydroxy*-2-p-*methoxybenzoyl*-3-*methylcoumarone* (III; R′ = H, R″ = C$_6$H$_4$·OMe), m. p. 177°, and not 6-hydroxy-5-*p*-methoxybenzoyl-3-methylcoumarone (cf. Karrer *et al.*, *loc. cit.*). The authentic specimen of (III; R′ = H, R″ = C$_6$H$_4$·OMe) was prepared by the interaction of 4-*o*-benzylresacetophenone with ω-bromoacetylanisole and subsequent debenzylation of the resulting 6-*benzyloxy*-2-p-*methoxybenzoyl*-3-*methylcoumarone* (III; R′ = Ph•CH$_2$, R″ = C$_6$H$_4$•OMe).

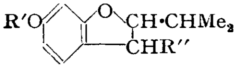


(VIII.)



(IX.)

(X.)



(XI.)

The interaction of two molecular proportions of methylmagnesium iodide with *ethyl* 6-*benzyloxycoumarone*-2-*carboxylate* (VIII; R′ = OEt) gave rise to 6-*benzyloxy*-2-(1-*hydroxy*iso-*propyl*)*coumarone* (IX), but when the ester (VIII; R′ = OEt) was replaced by the ketone (VIII, R′ = Me) and an excess of the Grignard reagent employed 6-*benzyloxy*-2-iso*propenyl*-*coumarone* (X) was obtained. Hydrogenation of the latter compound with a palladium–charcoal catalyst was accompanied by debenzylation, giving 6-hydroxy-2-*iso*propylcoumaran (XI; R′ = R″ = H), identical with an authentic sample. This preparation of (XI; R = R″ = H), which is more convenient than the earlier procedure described in Part V (*loc. cit.*), affords additional confirmatory evidence for the structure of euparin (Part V) and of the isomeric 6-hydroxy-2 : 2-dimethylchroman (*J.*, 1937, 1542). In the course of exploratory experiments the synthesis of 6-*methoxy*-3-*methyl*-2-iso*propylcoumaran* (XI; R′ = R″ = Me) was effected by way of 6-*methoxy*-3-*methyl*-2-iso*propenylcoumarone* by the action of an excess of methylmagnesium iodide on ethyl 6-methoxy-3-methylcoumaronecarboxylate followed by hydrogenation of the resulting *iso*propenyl derivative. The latter compound reacted with maleic anhydride to give an adduct.

EXPERIMENTAL.

6-*Methoxy*-2-*acetyl*-3-*methylcoumarone* (III; R′ = R″ = Me).—(*A*) Interaction of 6-methoxy-3-methylcoumarone (5 g.), methyl cyanide (5 ml.), and zinc chloride (3 g.) in ether (100 ml.) saturated with hydrogen chloride during 2 days gave a greenish product which was well washed with ether and dissolved in water (100 ml.). This solution was almost neutralised with ammonia, and then heated on the steam-bath for 15 minutes, giving a yellow solid from which 6-*methoxy*-2-*acetyl*-3-*methylcoumarone* was extracted with boiling light petroleum (b. p. 40—60°) (200 ml.) and then recrystallised from dilute alcohol, forming colourless prisms (4 g.), m. p. 77°, readily soluble in alcohol, benzene, or ether (Found : C, 70·3; H, 5·7; *M*, 215. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%; *M*, 204). On being warmed the yellow-green solution of the ketone in concentrated sulphuric acid became red and then violet. The 2 : 4-*dinitrophenylhydrazone* separated from acetic acid in crimson needles, m. p. 260° (Found : N, 14·6. $C_{18}H_{16}O_6N_4$ requires N, 14·6%).

(*B*) Acetyl chloride (2·5 g.) was added dropwise to a well stirred mixture of 6-methoxy-3-methylcoumarone (5 g.), stannic chloride (5 g.), and carbon disulphide (70 ml.) maintained at 0°. After having been kept at room temperature for one hour the mixture was decomposed with ice (200 g.), treated with sodium carbonate to neutralise the greater part of the hydrochloric acid, warmed on the steam-bath for ½ hour, and mixed with dilute hydrochloric acid (50 ml.). The carbon disulphide layer was subsequently combined with ethereal extracts of the aqueous liquor and the mixture washed with dilute hydrochloric acid and then aqueous sodium hydrogen carbonate, dried, and evaporated. Distillation of the residue in a vacuum gave 6-methoxy-2-acetyl-3-methylcoumarone which formed prisms (3·4 g.), m. p. and mixed m. p. 77°, from dilute alcohol.

(*C*) A mixture of 4-*O*-methylresacetophenone (20 g.), chloroacetone (18 g.), potassium carbonate (30 g.), and acetone (150 ml.) was refluxed for 15 hours with the addition of more chloroacetone (9 g.) and carbonate (10 g.) after 10 hours. The product was extracted with boiling light petroleum (b. p. 60—80°), the extracts were evaporated, and the residue (21 g.) was heated under reflux (oil-bath at 160°) with acetic anhydride (140 ml.) and sodium acetate (48 g.) for ½ hour and poured into water (800 ml.). 4 Days later extraction of the resulting dark viscous semi-solid with light petroleum (b. p. 60—80°) gave 6-methoxy-2-acetyl-3-methylcoumarone, m. p. and mixed m. p. 77°, after recrystallisation from dilute alcohol.

6-*Hydroxy*-2-*acetyl*-3-*methylcoumarone* (III; R′ = H, R″ = Me).—A solution of 6-hydroxy-3-methylcoumarone (1 g.) and methyl cyanide (2 ml.) in ether (100 ml.) was slowly saturated with hydrogen chloride at room temperature, and next day the semi-solid product was well washed with ether and dissolved in water (150 ml.). After having been treated with ammonia until only faintly acid to Congo-red this solution was heated on the steam-bath for 20 minutes and next day the resulting 6-*hydroxy*-2-*acetyl*-3-*methylcoumarone* was collected, well washed, dried, and crystallised from toluene and then dilute alcohol, forming faintly yellow flat parallelograms (0·7 g.), m. p. 172—173° (Found : C, 69·5; H 5·6. $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·8%). This ketone, which is easily soluble in ethyl acetate or alcohol and sparingly soluble in carbon tetrachloride or light petroleum, did not give a ferric reaction in alcohol. On being warmed the green solution of the compound in sulphuric acid became red and then purple. The 2 : 4-*dinitrophenylhydrazone* separated from acetic acid in crimson needles, m. p. 283° (decomp.) (Found : N, 15·0. $C_{17}H_{14}O_6N_4$ requires N, 15·1%).

Methylation of the foregoing keto-coumarone (0·5 g.) with methyl iodide (1 ml.) and potassium carbonate (2 g.) in boiling acetone (50 ml.) for 3 hours gave rise to 6-methoxy-2-acetyl-3-methylcoumarone (III; R′ = R″ = Me) which formed prisms (0·4 g.), m. p. 77°, from dilute alcohol and was identical in every way with the authentic specimen. The 2 : 4-dinitrophenylhydrazone had m. p. and mixed m. p. 260° (decomp.) and the *semicarbazone* formed colourless rectangular plates, m. p. 269°, from methanol, identical with a specimen prepared from the authentic ketone (Found : N, 16·2. $C_{13}H_{15}O_3N_3$ requires N, 16·1%).

2-(6'-*Methoxy*-3'-*methylcoumaron*-2'-*yl*)*benzopyrylium Chloride*.—Condensation of salicylaldehyde (0·6 g.) and 6-methoxy-2-acetyl-3-methylcoumarone (0·5 g.) in ethyl acetate (15 ml.) with an excess of hydrogen chloride followed by the addition of ether (50 ml.) next day gave the *chloride* which was collected, washed with ether, and crystallised from 1% hydrochloric acid, forming tiny amethyst prisms (0·3 g.) (Found : C, 70·0; H, 4·8; Cl, 10·4. $C_{19}H_{15}O_3Cl$ requires C, 69·8; H, 4·6; Cl, 10·9%). The *perchlorate* separated from acetic acid in elongated slender purple needles having a violet reflex and forming a deep red solution in alcohol which became colourless on the addition of aqueous sodium acetate (Found : C, 58·0; H, 3·9. $C_{19}H_{15}O_7Cl$ requires C, 58·4; H, 3·7%).

In a similar manner 8-*methoxy*-2-(6'-*methoxy*-3'-*methylcoumaron*-2'-*yl*)*benzopyrylium chloride* was prepared from the ketocoumarone (0·5 g.) and *o*-vanillin (0·7 g.) and on crystallisation from 5% hydrochloric acid was obtained in slender violet prisms (0·3 g.), having a copper reflex (Found : C, 67·0; H, 5·0; Cl, 10·6. $C_{20}H_{17}O_4Cl$ requires C, 67·3; H, 4·8; Cl, 10·0%). The perchlorate formed slender red prisms from acetic acid.

6-*Hydroxy*-2-*benzoyl*-3-*methylcoumarone* (III; R' = H, R'' = Ph).—This compound, m. p. 158—159°, was prepared from 6-hydroxy-3-methylcoumarone by Hoesch's method as described by Karrer and Widmer (*loc. cit.*), and on benzylation by means of an excess of benzyl bromide and potassium carbonate gave the 6-*benzyloxy*-2-*benzoyl*-3-*methylcoumarone* (III, R' = Ph·CH$_2$, R'' = Ph), m. p. 77°, identical in every way with an authentic specimen prepared by the following procedure. A mixture of 4-*O*-benzylresacetophenone (Gulati *et al.*, *J.*, 1934, 1765) (5 g.), ω-bromoacetophenone (6 g.), potassium carbonate (15 g.), and acetone (120 ml.) was heated under reflux for 20 hours, and on isolation the benzyl ether crystallised from alcohol in rosettes of colourless needles (4 g.), m. p. 77° (Found : C, 80·5; H, 5·4. $C_{23}H_{18}O_3$ requires C, 80·7; H, 5·3%). The 2 : 4-*dinitrophenylhydrazone* formed red needles, m. p. 250°, from nitrobenzene–alcohol (Found : N, 10·6. $C_{29}H_{22}O_6N_4$ requires N, 10·7%).

An authentic specimen of 6-benzyloxy-2-benzoyl-3-methylcoumarone was debenzylated by being heated under reflux with a mixture of equal volumes of acetic acid and concentrated hydrochloric acid for one hour, the benzyl chloride was removed with a current of steam, and the resulting 6-hydroxy-2-benzoyl-3-methylcoumarone was isolated from the residual liquor by means of ether and purified from non-phenolic material by means of dilute aqueous sodium hydroxide. Crystallised from ligroin, the hydroxy-coumarone formed yellow prisms, m. p. and mixed m. p. 158—159°, identical with a specimen prepared by Hoesch's method.

Methylation of 6-hydroxy-2-benzoyl-3-methylcoumarone by the methyl iodide–potassium carbonate method or by the methyl sulphate method gave 6-*methoxy*-2-*benzoyl*-3-*methylcoumarone* which was purified by distillation in a high vacuum and then by crystallisation from methanol, forming colourless prisms, m. p. 76° (Found : 76·5; H, 5·1. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%).

6-*Hydroxy*-5-*benzoyl*-3-*methylcoumaran* (VI).—Aluminium chloride (5·5 g.) was added in small portions to a well stirred mixture of 6-hydroxy-3-methylcoumaran (Part VII, *loc. cit.*) (2 g.), nitrobenzene (50 ml.), and benzoyl chloride (3·5 g.) in the course of 10 minutes. The stirring was stopped after 2 hours and 48 hours later the mixture was poured on ice, the product and nitrobenzene were extracted with ether, the combined extracts were evaporated, the nitrobenzene was removed with a current of steam, the residual liquor was cooled, and the crystalline product was isolated by filtration. Recrystallised from alcohol, the resulting 6-*hydroxy*-5-*benzoyl*-3-*methylcoumaran* formed almost colourless needles, m. p. 172°, which gave an intense red ferric reaction in alcohol (Found : C, 75·7; H, 5·7. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%).

6-*Hydroxy*-2-p-*methoxybenzoyl*-3-*methylcoumarone* (III; R' = H, R'' = C$_6$H$_4$·OMe).—The interaction between 4-*O*-benzylresacetophenone (4 g.), ω-bromoacetylanisole (Kunckel and Scheven, *Ber.*, 1898, **31**, 173) (5 g.), and potassium carbonate (15 g.) in boiling acetone was complete in 3 hours; a test portion did not then give a ferric reaction. On isolation the resulting 6-*benzyloxy*-2-p-*methoxybenzoyl*-3-*methylcoumarone* crystallised from benzene and then ethyl acetate in almost colourless prisms (3·5 g.), m. p. 160—161°, nearly insoluble in alcohol, sparingly soluble in chloroform, and having a vermilion sulphuric acid reaction changing to crimson when the mixture was warmed (Found : C, 77·3; H, 5·5. $C_{24}H_{20}O_4$ requires C, 77·4; H, 5·4%). The 2 : 4-*dinitrophenylhydrazone* formed crimson rectangular plates, m. p. 232°, from ethyl acetate (Found : N, 10·4. $C_{30}H_{24}O_7N_4$ requires N, 10·1%).

A solution of the foregoing benzyl ether (1 g.) in acetic acid (20 ml.) and concentrated hydrochloric acid (15 ml.) was boiled for an hour, the benzyl chloride was removed with steam, and the resulting 6-*hydroxy*-2-p-*methoxybenzoyl*-3-*methylcoumarone* was isolated with ether and purified by means of dilute aqueous sodium hydroxide. Crystallised from chloroform, the hydroxy-ketone was obtained in pale yellow plates (0·4 g.), m. p. 177—178°, which formed a deep yellow solution with aqueous sodium hydroxide and had a negative ferric reaction in alcohol (Found : C, 72·6; H, 5·1. $C_{17}H_{14}O_4$ requires C, 72·4; H, 5·0%). Methylation of this compound (1 g.) by the methyl iodide–potassium carbonate method gave 6-*methoxy*-2-p-*methoxybenzoyl*-3-*methylcoumarone* which formed colourless plates (0·65 g.), m. p. 142°, from alcohol, having a scarlet-red sulphuric acid reaction (Found : C, 73·1; H, 5·6. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%).

The foregoing hydroxy-ketone was identical with a specimen prepared by means of the Hoesch reaction as follows. A solution of 6-hydroxy-3-methylcoumarone (1 g.) and *p*-methoxyphenyl cyanide (1·2 g.) in ether (150 ml.) containing zinc chloride (2 g.) was saturated with hydrogen chloride at room temperature. Next day the passage of hydrogen chloride was continued for 2 hours and 24 hours later the mixture was treated with ether (150 ml.), the solvent was decanted, and the residual greenish semi-solid was well washed with fresh solvent and dissolved in water (150 ml.). This acidic solution was almost neutralised with aqueous sodium hydrogen carbonate and then heated on the steam-bath for ½ hour, giving a yellow precipitate of 6-hydroxy-2-*p*-methoxybenzoyl-3-methylcoumarone which was purified from non-phenolic material by means of dilute aqueous sodium hydroxide. A hot ethyl acetate extract (30 ml.) of the product was diluted with light petroleum (b. p. 80—100°) (20 ml.), boiled with charcoal, filtered, and evaporated. Crystallisation of the residue from ethyl acetate gave the hydroxy-ketone in rosettes of pale yellow needles (0·25 g.), m. p. 177°, identical with an authentic specimen (compare Karrer *et al.*, *loc. cit.*). Methylation of this material gave 6-methoxy-2-*p*-methoxybenzoyl-3-methylcoumarone, m. p. and mixed m. p. 142° (Found : C, 72·9; H, 5·5%).

6-*Benzyloxy*-2-(1-*hydroxy*iso*propyl)coumarone* (IX).—A solution of ethyl 6-benzyloxycoumarone-2-carboxylate (Part VII, *J.*, 1948, 2254) (4 g.) in ether (250 ml.) was gradually added to well stirred methylmagnesium iodide (from 0·75 g. of magnesium and 3 g. of methyl iodide) in ether (25 ml.) cooled with ice-water, and the yellow solution heated under reflux on the steam-bath for 20 minutes, cooled, and treated with dilute hydrochloric acid. The ethereal layer was separated, washed with aqueous sodium hydrogen carbonate, dried, and evaporated, and the residue crystallised from dilute alcohol, giving 6-*benzyloxy*-2-(1-*hydroxy*iso*propyl)coumarone* (2·5 g.) in long colourless needles, m. p. 74°, readily soluble in alcohol, benzene, or ethyl acetate and sparingly soluble in light petroleum (Found : C, 76·8; H, 6·5; *M*, 290. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%; *M*, 282).

6-*Benzyloxy*-2-*acetylcoumarone* (VIII; R′ = Me).—A mixture of 4-*O*-benzyl-*β*-resorcylaldehyde (10 g.), potassium hydroxide (2·5 g.), alcohol (60 ml.), and chloroacetone (4·5 g.) was heated under reflux for ½ hour, and, after the addition of water (100 ml.), the greater part of the alcohol was evaporated and the cooled residue extracted with ether. Evaporation of the solvent from the dried extracts left the *ketone* (VIII; R′ = Me) which was purified by distillation in a vacuum, b. p. 130°/0·01 mm., and then by crystallisation from dilute alcohol, forming colourless plates (7·5 g.), m. p. 98°, readily soluble in benzene or ethyl acetate (Found : C, 76·4; H, 5·4. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%). The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate in scarlet needles, m. p. 248° (Found : N, 12·7. $C_{23}H_{18}O_6N_4$ requires N, 12·6%).

6-*Hydroxy*-2-iso*propylcoumaran* (XI; R′ = R″ = H).—A solution of the foregoing ketone (4 g.) in ether (100 ml.) was slowly added to ethereal methyl magnesium iodide (from 1·5 g. of magnesium, 8 g. of methyl iodide, and 100 ml. of ether) cooled with ice-water, and the mixture was heated on the steam-bath for ½ hour. On isolation the product was distilled in a high vacuum, b. p. 160°/0·004 mm., and then crystallised from alcohol giving 6-*benzyloxy*-2-iso*propenylcoumarone* (X) in colourless plates (1·5 g.), m. p. 91—92°, soluble in benzene or ethyl acetate (Found : C, 81·9; H, 6·3. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%). Hydrogenation of this diene (0·5 g.), dissolved in methanol (100 ml.), with hydrogen and a palladium–charcoal catalyst (from 0·1 g. of palladium chloride and 1 g. of charcoal) gave rise to 6-hydroxy-2-*iso*propylcoumaran which was purified by distillation in a vacuum, b. p. 105°/0·03 mm., and then by crystallisation from light petroleum (b. p. 60—80°), forming colourless rhombic prisms (0·3 g.), m. p. 79°, identical in every way with the specimen described in Part V (*J.*, 1939, 933).

6-*Methoxy*-3-*methyl*-2-iso*propylcoumaran* (XI; R′ = R″ = Me).—Interaction of ethyl 6-methoxy-3-methylcoumarone-2-carboxylate (5 g.) in ether (200 ml.) with methylmagnesium iodide (from 1·5 g. of magnesium, and 5 g. of methyl iodide) at 0° and then by heating under reflux for 45 minutes, and decomposition of the reaction product with dilute hydrochloric acid gave rise to 6-*methoxy*-3-*methyl*-2-iso*propenylcoumarone*. Purified by distillation in a vacuum and then by crystallisation from light petroleum (b. p. 40—60°), the compound formed irregular prisms (3·2 g.), m. p. 69°, soluble in alcohol or benzene (Found : C, 77·1; H, 6·8. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%). On being heated with maleic anhydride (1 g.) in benzene (2·5 ml.) for 16 hours this (0·5 g.) gave an adduct which was purified by sublimation in a vacuum and then by crystallisation from ethyl acetate–light petroleum (b. p. 80—100°), forming colourless prisms, m. p. 147—148°.

Hydrogenation of 6-methoxy-3-methyl-2-*iso*propenylcoumarone (1·5 g.), dissolved in methanol (100 ml.), with hydrogen and a palladium–charcoal catalyst (from 0·1 g. of palladium chloride and 1 g. of charcoal) was complete in one hour. On isolation 6-*methoxy*-3-*methyl*-2-iso*propylcoumaran* (XI; R′ = R″ = Me) was obtained as a colourless viscous oil (0·4 g.), b. p. 85°/0·05 mm. (Found : C, 75·9; H, 8·9. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·7%).

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