

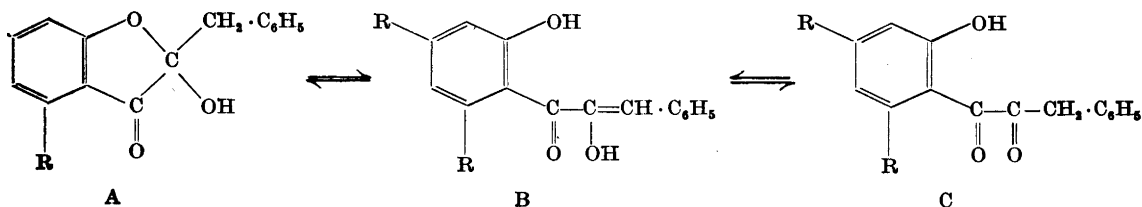
Confirmation of the Structure of 2-Benzyl-2-hydroxycoumaran-3-ones

CARL ENEBÄCK and JARL GRIPENBERG

Department of Chemistry, Institute of Technology, Helsingfors, Finland

A number of hydroxy and methoxy derivatives of 2-benzylcoumaran-3-one, chalcone and 1,3-diphenylpropane-1,2-dione, corresponding to the tautomeric forms of 2-benzyl-2-hydroxycoumaran-3-ones¹, have been prepared. A comparison of the ultra-violet spectra and the carbonyl frequencies in the infra-red shows definitely the correctness of the 2-benzyl-2-hydroxycoumaran-3-one structure.

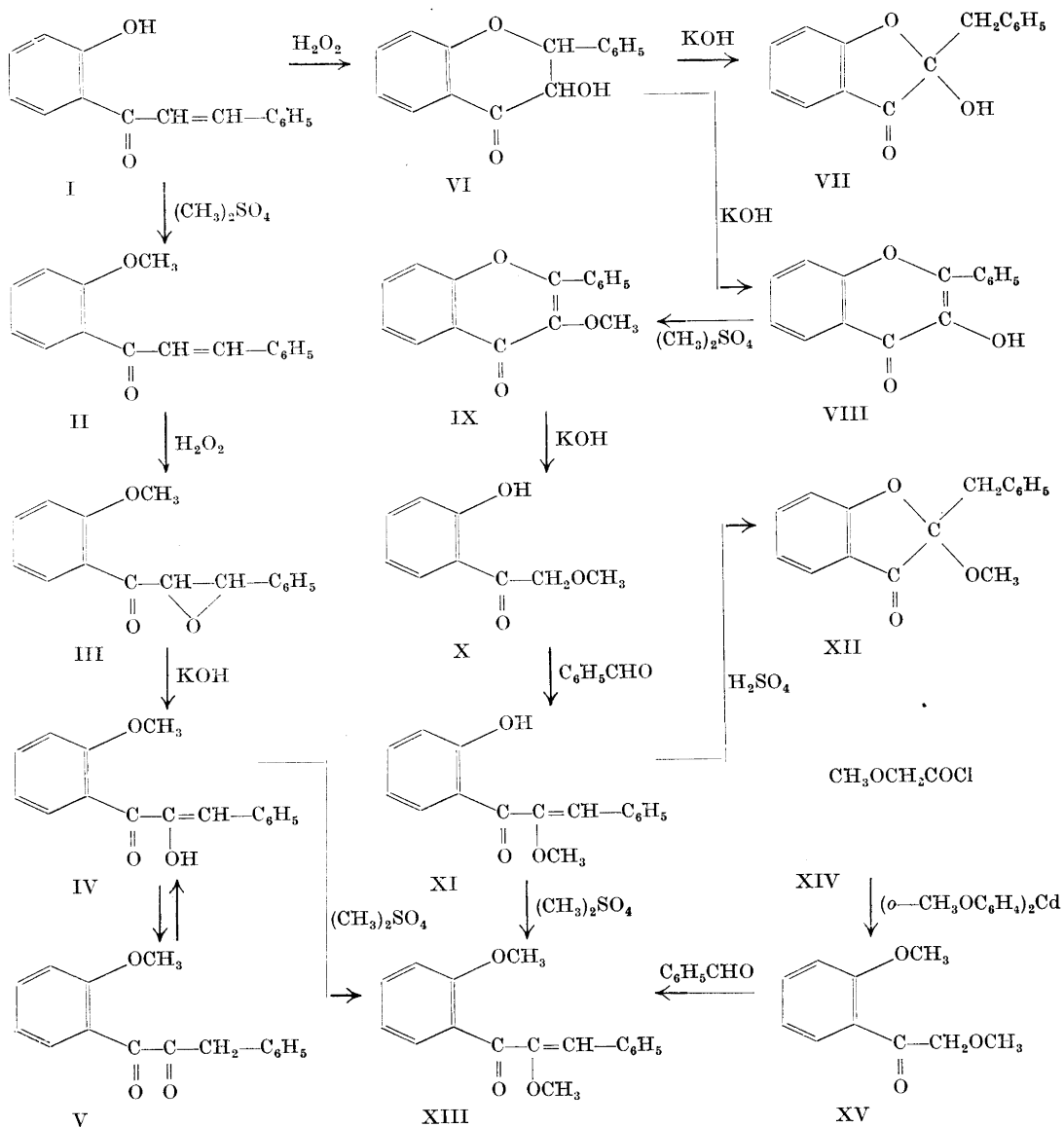
Some years ago, one of the present authors showed that a number of substances, earlier formulated as 3-hydroxyflavanones¹, were in all probability 2-benzyl-2-hydroxycoumaran-3-ones, a conclusion arrived at independently by Kubota² also. It was emphasised that the 2-benzyl-2-hydroxycoumaran-3-one(A) can be tautomeric with the hydroxychalcone (B) and the diketone (C)



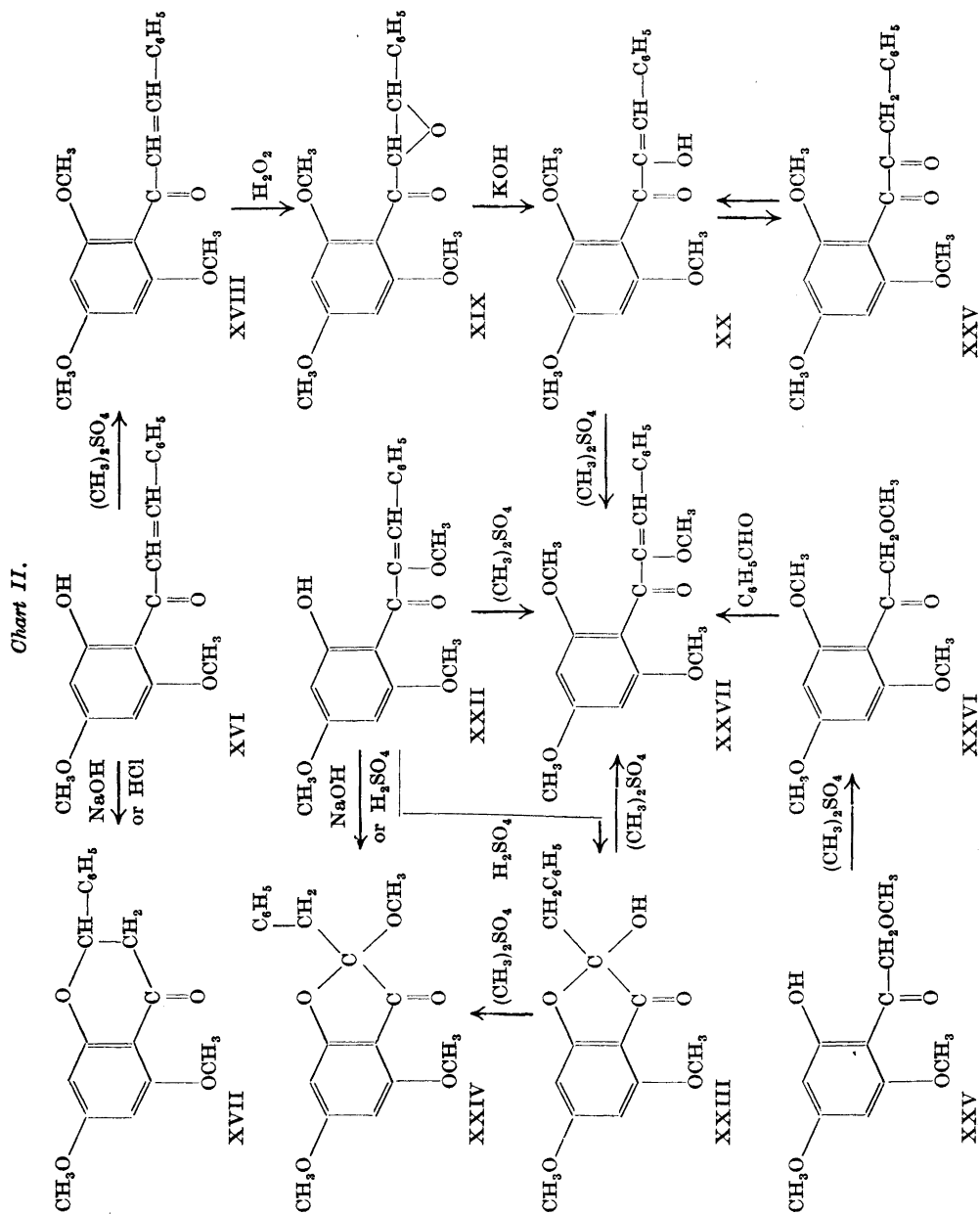
The structure A could not be considered as definitely established, because of the possibility that this tautomeric shift takes place during the reactions used in the determination of structure.

It was therefore decided to try to find further support for this formula from a comparison of the ultra-violet and infra-red spectra with those of compounds corresponding to the three tautomeric forms A, B and C, but where the tautomeric shift is made impossible. This can be achieved either by methylation of the hydroxyls or by removing them. The latter method is permissible only if the hydroxyl is in such a position that it does not have any influence on the spectral properties of the compound in question.

Chart I



Reference has already been made¹ to one case, where the ultra-violet spectrum could be taken as support for the 2-benzyl-2-hydroxycoumaran-3-one structure.



Of the three tautomeric structures, A and C can give rise to one methyl ether, whereas two monomethyl ethers and one dimethyl ether can be derived from B. All these methyl derivatives in the two series, where R = H and

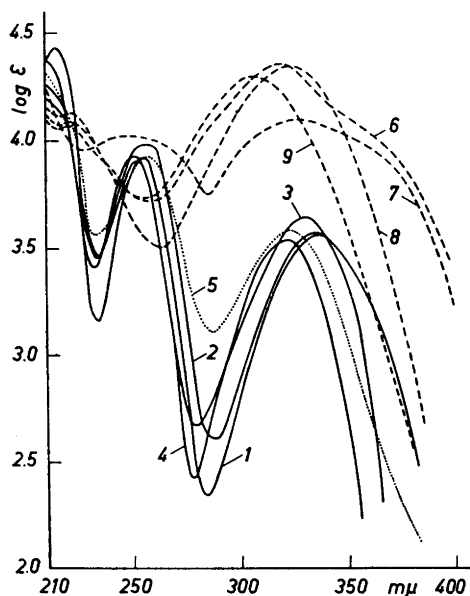


Fig. 1. Spectra of: 1. 2-Benzyl-2-hydroxycoumaran-3-one(VII), 2. 2-Benzyl-2-methoxycoumaran-3-one(XII), 3. 2-Benzylcoumaran-3-one, 4. Flavanone, 5. 1-(2-Methoxyphenyl)-3-phenylpropane-1,2-dione(V), 6. 2'-Hydroxychalcone(I), 7. 2'-Hydroxy- α -methoxychalcone(XI), 8. α -Hydroxy-2'-methoxychalcone(IV), 9. α ,2'-Dimethoxychalcone(XIII) (all in ethanol).

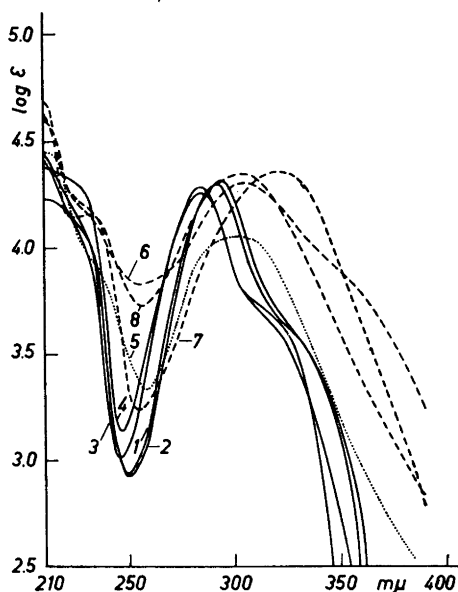


Fig. 2. Spectra of: 1. 2-Benzyl-2-hydroxy-4,6-dimethoxycoumaran-3-one(XXIII), 2. 2-Benzyl-2,4,6-trimethoxycoumaran-3-one(XXIV), 3. 2-Benzyl-4,6-dimethoxycoumaran-3-one, 4. 5,7-Dimethoxyflavanone(XVII), 5. 1-(2,4,6-Trimethoxyphenyl)-3-phenylpropane-1,2-dione(XXI), 6. 2'-Hydroxy- α ,4',6'-trimethoxychalcone(XXII), 7. α -Hydroxy-2',4',6'-trimethoxychalcone(XX), 8. α ,2',4',6'-Tetramethoxychalcone(XXVII) (all in ethanol).

OCH₃, respectively, have been synthesised. The syntheses are outlined in Chart I and Chart II, which show the interrelationships between the different compounds, which serve to establish their structures.

The details of these reactions are given in the experimental part, but the following points require some further comments. Ring closure of 2'-hydroxychalcones to flavanones both by acids and by very dilute alkali is well established^{3,4}. However, this does not hold when there is a methoxyl group in the α -position of the chalcone (*Cf.*, however Robertson *et al.*⁵). The formation of a 2-benzyl-2-hydroxycoumaran-3-one, when such a chalcone is treated with acids¹ was the starting point for this work, but it has now also been observed that the corresponding methoxy derivative is formed as well (*e. g.*, XXIV from XXII). A similar observation has been made also by Tsukamoto and Tomi-naga⁶. When 2'-hydroxy- α -methoxychalcone (XI) was treated in the same way only a neutral compound was obtained. This is thought to be 2-benzyl-2-methoxycoumaran-3-one (XII). Methylation of 2-benzyl-2-hydroxycoumaran-

3-one (VII) was expected to give the same compound, which should have confirmed its structure, but unfortunately all attempts to methylate VII failed. The structure of XII is therefore somewhat uncertain, although it is difficult to imagine any other structure, which could explain its properties.

It was further found that treatment of XXII with dilute alkali also gave XXIV, whereas XI was recovered unchanged from similar treatment.

The transformation of the enols IV and XX into the corresponding diketones V and XXI was achieved by distilling them in the presence of piperidine⁷. The enol was regenerated when an alkaline solution of the diketone was acidified.

The ultra-violet spectra of the different methyl derivatives and some other relevant compounds of the two series, where R = H and R = OCH₃ are reproduced in Figs. 1 and 2, respectively. (The spectra of compounds corresponding to the three structures A, B and C are drawn with different markings.)

From Fig. 1 it can be seen that the spectra of 2-benzyl-coumaran-3-one, 2-benzyl-2-hydroxycoumaran-3-one (VII), 2-benzyl-2-methoxycoumaran-3-one (XII) and flavanone are all very similar, but also that the spectrum of 1-(2-methoxyphenyl)-3-phenylpropane-1,2-dione (V) does not differ very much. The spectra of the chalcones IV and XIII are of a different type and close to that of I and chalcone (not shown in the figure).

The spectrum of 2'-hydroxy- α -methoxychalcone (XI) deserves further consideration, because it differs significantly from those of the other chalcones in having a maximum at 250 m μ , where the other have a minimum and having instead a minimum at 285 m μ . It thus shows some resemblance to the spectra of compounds with the *o*-hydroxyacetophenone chromophore. We would like to offer the following explanation for this difference (*Cf.* Black and Lutz⁸). Models show that when there is a methoxyl group in the α -position, the cinnamoyl group of the chalcone can be coplanar only if the other aromatic ring is out of this plane. In 2'-hydroxy- α -methoxychalcone the hydrogen bond between the hydroxyl and the carbonyl will, however, keep the carbonyl coplanar with this aromatic ring, whereby the coplanarity of the cinnamoyl group will be disturbed. The spectrum will therefore be more close to that of *o*-hydroxyacetophenone, than that of the other chalcones, where the cinnamoyl group will be the dominating factor.

From Fig. 2 it is obvious again that the spectra of the benzylcoumaranones are very close to that of the corresponding flavanone XVII, but in this case the diketone XXI differs clearly by the absence of the inflexion at 310—320 m μ . The spectra of the chalcones are very similar to those of the first series, but the difference between the chalcones on the one hand and the flavanones and benzylcoumaranones on the other hand is not so pronounced here. There is in this case no anomaly in the spectrum of 2'-hydroxy- $\alpha,4',6'$ -trimethoxychalcone (XXII), although there is the same reason to expect a noncoplanarity of the cinnamoyl group as in XI. In this case, however, the absorption of the *o*-hydroxyacetophenone chromophore lies so close to that of the chalcones that it would not show up as a separate maximum.

As regards the tautomeric possibilities set forth in the beginning of this paper, it can be concluded that these spectra support strongly the benzyl-

hydroxycoumaranone structure (A), but that, particularly in the unsubstituted series, the diketone structure (C) cannot be definitely excluded. The spectra of the chalcones differ enough to make the structure B highly improbable.

In order to get more support for structure A the carbonyl frequencies in the infra-red were determined in chloroform solution (Table 1).

Table 1.

Compound	CO frequency cm^{-1}	Compound	CO frequency cm^{-1}
2-Benzyl-2-hydroxycoumaran-3-one (VII)	1 730	2-Benzyl-2-hydroxy-4,6-dimethoxycoumaran-3-one (XXIII)	1 706
2-Benzyl-2-methoxycoumaran-3-one (XII)	1 720	2-Benzyl-2,4,6-trimethoxycoumaran-3-one (XXIV)	1 696
2-Benzylcoumaran-3-one	1 713	2-Benzyl-4,6-dimethoxycoumaran-3-one ¹	1 690
Flavanone	1 695 ⁹	5,7-Dimethoxyflavanone (XVII)	1 665
3-Hydroxyflavanone (VI)	1 697	1-(2,4,6-Trimethoxyphenyl)-3-phenylpropane-1,2-dione (XXI)	1 710
1-(2-Methoxyphenyl)-3-phenylpropane-1,2-dione (V)	1 716 1 660	$\alpha,2'4',6'$ -Tetramethoxychalcone (XXVII)	1 656 1 650
$\alpha,2'$ -Dimethoxychalcone (XIII)	1 650	α -Hydroxy-2',4',6'-trimethoxychalcone (XX)	1 666
α -Hydroxy-2'-methoxychalcone (IV)	1 655	2'-Hydroxy- $\alpha,4',6'$ -trimethoxychalcone (XXII)	1 625
2'-Hydroxy- α -methoxychalcone (XI)	1 619		

All the coumaranone and flavanone derivatives in the series where $R = \text{OCH}_3$ have the carbonyl band at lower wave-numbers (24–30 cm^{-1}) than the corresponding compound in the unsubstituted series, in accord with expectation¹⁰. There is also a difference in the same direction between the diketones XXI and V but much smaller (4 and 6 cm^{-1} in the two bands). In the chalcone derivatives the differences are also small, but in the opposite direction. It should, however, be noted that the values for the chalcones are obtained from measurements in two different laboratories. The low values for XI and XXII are of course due to the hydrogen bond between the 2'-hydroxy group and the carbonyl¹⁰.

The carbonyl frequency of a compound with structure B should be similar to XI and XXII, whereas a compound with structure C should show two carbonyl bands, one around 1 710 cm^{-1} , the other around 1 625 cm^{-1} . Instead the compounds VII and XXIII show only one carbonyl band close to that found in other coumaranone derivatives. The reason why the hydroxyl and, to a lesser extent, the methoxyl group in the 2-position of the benzylcoumaranones shifts the carbonyl frequency to higher wave-numbers is not clear, but it seems to be typical of these compounds.

The structure A must thus be correct, although the possibility that very small amounts of B and/or C exist in equilibrium in solution cannot be excluded on the present evidence. The infra-red data serve also to confirm the impossibility of a 3-hydroxyflavanone structure ¹.

EXPERIMENTAL

(The analyses have been performed by Dr. A. Bernhardt, Mülheim, Germany.)

2'-Hydroxychalcone (I) was prepared according to Feuerstein and v. Kostanecki ¹¹. λ_{\max} 222 $m\mu$ (log ϵ 4.09), 318 $m\mu$ (log ϵ 4.37), 355 $m\mu$ (infl.) (log ϵ 4.09), λ_{\min} 216 $m\mu$ (log ϵ 4.07), 258 $m\mu$ (log ϵ 3.72).

2'-Methoxychalcone (II). *2'-Hydroxychalcone* (I) (9 g) was methylated with dimethyl sulphate (3.9 ml) in acetone (100 ml) in the presence of potassium carbonate (10 g). Filtration and removal of the acetone was followed by washing the ether solution of the product with dilute sodium hydroxide and water. It was then twice distilled under vacuum, b. p. 214–215°/8 mm. (Yield 6.1 g). v. Auwers and Brink ¹² report b. p. 226°/11.5 mm.

2'-Methoxychalcone oxide (III). *2'-Methoxychalcone* (II) (6.1 g) was dissolved in methanol (50 ml) and the solution chilled in an ice-bath to +10°. Hydrogen peroxide (13 %; 9 ml) and 6 N potassium hydroxide (2.1 ml) were added, so that the temperature was kept below +35°. After a few minutes a voluminous precipitate of *2'-methoxychalcone oxide* was formed. This was recrystallised from methanol. Yield 5.8 g, colourless crystals, m. p. 125°. (Found: C 75.04; H 5.72. $C_{16}H_{14}O_3$ requires C 75.57; H 5.55).

α -Hydroxy-2'-methoxychalcone (IV). *2'-Methoxychalcone oxide* (III) (2.5 g) was dissolved in ethanol (25 ml). To this was added 1 N potassium hydroxide (15 ml) and the mixture was refluxed for half an hour. About half of the ethanol was distilled off from the dark red solution. The cooled solution was then acidified with 2 N hydrochloric acid (15 ml), which precipitated a viscous mass. This was separated and crystallised when treated with methanol. Recrystallisation from methanol gave light yellow leaflets, m. p. 133.5°, λ_{\max} 220 $m\mu$ (log ϵ 4.08), 234 $m\mu$ (infl.) (log ϵ 3.94), 325 $m\mu$ (log ϵ 4.36), λ_{\min} 263 $m\mu$ (log ϵ 3.51). (Found: C 75.25; H 5.64. $C_{16}H_{14}O_3$ requires C 75.57; H 5.55). It gives a strong brown-violet colour with ferric chloride. Jörlander ¹³ has prepared the same compound in a different way, but he gives m. p. 118°.

1-(2-Methoxyphenyl)-3-phenylpropane-1,2-dione (V). *α -Hydroxy-2'-methoxychalcone* (IV) (100 mg) was placed together with 0.5 ml of a solution of piperidine in hexane (1 g/l) in a test tube with a side arm. The mixture was heated in an oil bath. When all the hexane had evaporated, a cold finger was inserted and the tube evacuated to 0.25 mm. The temperature of the oil bath was now regulated so that a slow distillation of the diketone to the cold finger was achieved. It formed an oil drop, which upon treatment with methanol gave yellow crystals, m. p. 72°, λ_{\max} 259 $m\mu$ (log ϵ 3.93), 323 $m\mu$ (log ϵ 3.60), λ_{\min} 233 $m\mu$ (log ϵ 3.57), 287 $m\mu$ (log ϵ 3.11). It gives no colour with ferric chloride. It dissolves in warm sodium hydroxide and acidification of this solution regenerates the enol form (IV), m. p. 133°.

2'-Hydroxy- α -methoxychalcone (XI). 3-Hydroxyflavanone ¹⁴ (VI), m. p. 188° was converted into a mixture of 2-benzyl-2-hydroxy-coumaran-3-one (VII) (λ_{\max} 256 $m\mu$ (log ϵ 3.93), 336 $m\mu$ (log ϵ 3.58), λ_{\min} 234 $m\mu$ (log ϵ 3.16), 284 $m\mu$ (log ϵ 2.34)) and 3-hydroxyflavone (VIII) upon treatment with alkali ¹. The last mentioned was also obtained according to v. Kostanecki and Szabrański ¹⁵. Methylation of 3-hydroxyflavone with dimethyl sulphate and potassium carbonate in acetone gave 3-methoxyflavone (IX), m. p. 113°. Oyamada ¹⁶ reports m. p. 114°.

3-Methoxyflavone (4 g) was dissolved in 10 % potassium hydroxide in ethanol (100 ml) and the solution was refluxed for 4 h. Water (100 ml) was then added and the main part of the ethanol was distilled off. The remaining solution was extracted with ether and then acidified with acetic acid. The acid solution was extracted with ether, and the ether solution was washed with sodium hydrogen carbonate. Removal of the ether left 2-hydroxy- ω -methoxyacetophenone (X) (Cf. Ref.¹⁷) as an oil (1.5 g). This, without further purification, was dissolved in ethanol (15 ml) and benzaldehyde (2 ml), and 50 % sodium hydroxide (3 ml) were added. After standing for one day the solution was acidified with

2 N hydrochloric acid and extracted with ether. The ether solution was washed with sodium hydrogen carbonate and evaporated. The residue was crystallised from methanol and sublimed under vacuum, giving yellow needles of 2'-hydroxy- α -methoxychalcone, m.p. 52° (1.3 g), λ_{\max} 250 m μ (log ϵ 4.03), 323 m μ (log ϵ 4.12), λ_{\min} 227 m μ (log ϵ 3.96), 286 m μ (log ϵ 3.76). (Found: C 74.97; H 5.71. C₁₆H₁₄O₃ requires C 75.57; H 5.55).

2-Benzyl-2-methoxycoumaran-3-one (XII). 2'-Hydroxy- α -methoxychalcone (XI) (0.35 g) was boiled for 30 h with 2 N sulphuric acid (10 ml) in ethanol (50 ml). The ethanol was distilled off and the aqueous solution was extracted with ether. The ether solution was washed with sodium hydrogen carbonate and 2 N sodium hydroxide. Acidification of these washings gave only negligible amounts of material. The ether was removed, yielding an oil which soon crystallised. Recrystallisation from methanol gave 2-benzyl-2-methoxycoumaran-3-one (0.2 g) as colourless crystals, m. p. 50°, λ_{\max} 257 m μ (log ϵ 3.99), 337 m μ (log ϵ 3.56), λ_{\min} 233 m μ (log ϵ 3.45), 288 m μ (log ϵ 2.61). (Found: C 74.96; H 5.52; C₁₆H₁₄O₃ requires C 75.57; H 5.55). It gives no colour with magnesium and hydrochloric acid.

α ,2'-Dimethoxychalcone (XIII). a). α -Hydroxy-2-methoxychalcone (IV) (0.5 g) was dissolved in acetone (10 ml) and dimethyl sulphate (0.3 ml) and potassium carbonate (4 g) were added and the mixture refluxed for 4 h. The α ,2'-dimethoxychalcone (0.3 g), isolated in the usual way, was recrystallised from methanol, m. p. 55.5–56°, λ_{\max} 221 m μ (log ϵ 4.13), 307 m μ (log ϵ 4.31), λ_{\min} 215 m μ (log ϵ 4.11), 255 m μ (log ϵ 3.75). (Found C 76.06; H 6.42; C₁₇H₁₆O₃ requires C 76.10; H 6.01).

b) 2'-Hydroxy- α -methoxychalcone (XI) (0.3 g) was methylated in the same way as in a). Yield 0.2 g, m. p. 55–56°. It gives no depression of m. p. when mixed with material prepared according to a).

c) A benzene solution of bis-(*o*-methoxyphenyl)cadmium was prepared from *o*-bromoanisole (67 g) through the Grignard-compound. To this was added during 10 min methoxyacetyl chloride (XIV) (31 g), dissolved in benzene (53 ml). Heat was evolved and refluxing was continued for 15 min after the addition. The mixture was then poured into ice water (450 g) containing a little sulphuric acid. The benzene layer was separated, washed with sodium hydroxide and dried. Removal of the benzene left an oil from which 57 g of a fraction boiling at 88–182°/8 mm was obtained. 15 g of this fraction were treated with Girard-reagent-T (15 g) giving 2.3 g of ω ,2-dimethoxyacetophenone (XV) as an oil. This (1.9 g), without further purification, was kept with benzaldehyde (5 g) and 10 % sodium hydroxide in 50 % ethanol (50 ml) for 1 day at room temperature and then for some days in the refrigerator. The crystals that had separated (1.3 g) were recrystallised from methanol. M. p. 55–56°, alone or mixed with material prepared according to a) or b).

5,7-Dimethoxyflavanone (XVII). A hot solution of 2'-hydroxy-4',6'-dimethoxychalcone¹⁸ (XVI) (0.5 g) in ethanol (1.5 ml) was rapidly diluted with cold 1.5 % sodium hydroxide (15 ml). 5,7-Dimethoxyflavanone precipitated and was recrystallised from toluene, m. p. 145–146° (0.15 g). It gives no depression when mixed with material prepared from the same starting material by treatment with acid¹⁹. λ_{\max} 284 m μ (log ϵ 4.26), 315 m μ (infl.) (log ϵ 3.65), λ_{\min} 246 m μ (log ϵ 3.14).

2',4',6'-Trimethoxychalcone (XVIII). 2'-Hydroxy-4',6'-dimethoxychalcone¹⁸ (XVI) (4.5 g) was methylated with dimethyl sulphate (2.4 ml) in acetone (40 ml) in the presence of potassium carbonate (6 g). 2',4',6'-Trimethoxychalcone (3.25 g) was obtained after recrystallisation from methanol as yellow crystals, m. p. 84°. (Found: C 73.01; H 6.11; C₁₈H₁₈O₄ requires C 72.46; H 6.08).

2',4',6'-Trimethoxychalcone oxide (XIX). 2',4',6'-Trimethoxychalcone (XVIII) (2 g) was dissolved in methanol (20 ml). This was cooled in an ice bath and hydrogen peroxide (13 %; 2.3 ml) and 6 N potassium hydroxide (0.52 ml) were added so that the temperature did not rise above + 20°. After a few minutes the 2',4',6'-trimethoxychalcone oxide precipitated. It was recrystallised from methanol, giving colourless crystals (1.8 g), m. p. 106.5°. (Found: C 68.21; H 6.01; C₁₈H₁₈O₅ requires C 68.78; H 5.77).

α -Hydroxy-2',4',6'-trimethoxychalcone (XX). 2',4',6'-Trimethoxychalcone oxide (XIX) (1.25 g) was dissolved in ethanol (10 ml) and 1 N potassium hydroxide was added. The mixture was refluxed for half an hour. Acidification produced a viscous mass, which rapidly solidified. After recrystallisation from methanol α -hydroxy-2',4',6'-trimethoxychalcone was obtained as light yellow needles (0.8 g), m. p. 138–139°. Recrystallisation from light petroleum (b.p. 60–80°) gave a mixture of bipyramidal crystals of m. p. 120° and the needles of the higher melting form. λ_{\max} 230 m μ (log ϵ 4.17), 320 m μ (log ϵ 4.37),

λ_{\min} 222 μm (log ϵ 4.15), 255 μm (log ϵ 3.24). (Found: C 68.67; H 5.91; $\text{C}_{18}\text{H}_{16}\text{O}_5$ requires C 68.78; H 5.77). It gives a dark brown-violet colour with ferric chloride.

1-(2,4,6-Trimethoxyphenyl)-3-phenylpropane-1,2-dione (XXI). This compound was obtained from α -hydroxy-2',4',6'-trimethoxychalcone in exactly the same way as described above for the preparation of 1-(2-methoxyphenyl)-3-phenylpropane-1,2-dione from the corresponding enol. Recrystallisation from methanol gave bright yellow leaflets, m. p. 98°. λ_{\max} 303 μm (log ϵ 4.06), λ_{\min} 258 μm (log ϵ 3.35). It gives no colour with ferric chloride, but dissolves upon warming in 1 N sodium hydroxide. Acidification regenerates the enol (XX), m. p. 138°.

2'-Hydroxy- α ,4',6'-trimethoxychalcone (XXII) was prepared according to Kimura and Hoshi²⁰. M. p. 113°, λ_{\max} 230 μm (infl.) (log ϵ 4.18), 305 μm (log ϵ 4.31), λ_{\min} 255 μm (log ϵ 3.84).

2-Benzyl-2-hydroxy-4,6-dimethoxycoumaran-3-one¹ (XXIII) was prepared according to Lindstedt²¹ from 2'-hydroxy- α ,4',6'-trimethoxychalcone (XXII). λ_{\max} 290 μm (log ϵ 4.30), 322 μm (infl.) (log ϵ 3.66), λ_{\min} 249 μm (log ϵ 2.93).

2-Benzyl-2,4,6-trimethoxycoumaran-3-one (XXIV) a) 2-Benzyl-2-hydroxy-4,6-dimethoxycoumaranone (XXIII) (1.2 g) was methylated with dimethyl sulphate (0.57 ml) in acetone (18 ml) in the presence of potassium carbonate (2 g). The mixture was first allowed to stand 15 h at room temperature and then refluxed for 4 h. Treatment of the reaction mixture in the usual way gave a residue (1.2 g), which upon recrystallisation from methanol gave a mixture of colourless and yellow crystals. They were separated by hand picking, and further recrystallisation of the colourless crystals gave 2-benzyl-2,4,6-trimethoxycoumaran-3-one (0.57 g), m. p. 108–109°, λ_{\max} 293 μm (log ϵ 4.32), 325 μm (infl.) (log ϵ 3.66), λ_{\min} 251 μm (log ϵ 2.92). (Found: C 68.66; H 6.03; $\text{C}_{18}\text{H}_{16}\text{O}_5$ requires C 68.78; H 5.77). It gives no colour with magnesium and hydrochloric acid. The yellow crystals, m. p. 134–135°, were identified as α ,2',4',6'-tetramethoxychalcone (see below).

b) 2'-Hydroxy- α ,4',6'-trimethoxychalcone (XXII) (0.35 g) was dissolved in hot ethanol (0.75 ml). A cold 1.5 % sodium hydroxide solution (3.75 ml) was then added. The mixture was allowed to stand for 40 h, but no precipitation took place. After refluxing the mixture for one hour 2-benzyl-2,4,6-trimethoxycoumaran-3-one precipitated. Recrystallisation gave 0.13 g of m. p. 108–109°, not depressed by material prepared according to a).

c). In the preparation of 2-benzyl-2-hydroxy-4,6-dimethoxycoumaran-3-one (XXIII) according to Lindstedt²¹ the ether solution remaining after washing with alkali was evaporated leaving a residue, which after recrystallisation from hexane and then from methanol gave a small amount of 2-benzyl-2,4,6-trimethoxycoumaran-3-one, m. p. 107–108°, undepressed by material prepared according to a) or b).

α ,2',4',6'-Tetramethoxychalcone (XXVII). a). ω ,2,4,6-Tetramethoxyacetophenone (XXV) was prepared by methylation of ω -methoxyphloracetophenone²² (2 g) with dimethyl sulphate and potassium carbonate. It had m. p. 56.5–57°. (Slater and Stephen²² report 50°). 0.1 g of this was dissolved in ethanol (2.5 ml) and benzaldehyde (0.4 ml), 10 % sodium hydroxide (2.5 ml) was added and the mixture allowed to stand at room temperature. Next day the yellow crystals of α ,2',4',6'-tetramethoxychalcone were filtered off and recrystallised from methanol. Yield 0.1 g, m. p. 134–135°, λ_{\max} 227 μm (infl.) (log ϵ 4.23), 303 μm (log ϵ 4.35), λ_{\min} 255 μm (log ϵ 3.73). (Found: C 69.41; H 6.10; $\text{C}_{19}\text{H}_{20}\text{O}_5$ requires C 69.50; H 6.13).

b). α -Hydroxy-2',4',6'-trimethoxychalcone (XX) (0.5 g) was methylated with dimethyl sulphate and potassium carbonate, giving 0.4 g of α ,2',4',6'-tetramethoxychalcone, m. p. 135°.

c). 2'-Hydroxy- α ,4',6'-trimethoxychalcone (XXII) (1 g) was methylated with dimethyl sulphate and potassium carbonate, giving 0.7 g of α ,2',4',6'-tetramethoxychalcone, m. p. 134–135°.

d). The yellow crystals obtained by methylation of 2-benzyl-2-hydroxy-4,6-dimethoxycoumaran-3-one (XXIII), m. p. 134–135° gave no depression when mixed with material prepared according to a), b) or c), which also gave no depression of m. p. when mixed.

2-Benzylcoumaran-3-one, was prepared according to v. Auwers²³ from ethyl 3-hydroxycoumaron-2-carboxylate. v. Auwers describes 2-benzylcoumaran-3-one as an oil, but in our hands the oil first obtained solidified after standing for some time. It had m. p. 50° but appeared to be still somewhat impure, because its infra-red spectrum shows a weak

peak at 1750 cm^{-1} , attributable to an ester group. $\lambda_{\text{max}} 252\text{ m}\mu$ ($\log \epsilon 3.94$), $330\text{ m}\mu$ ($\log \epsilon 3.64$), $\lambda_{\text{min}} 231\text{ m}\mu$ ($\log \epsilon 3.41$), $278\text{ m}\mu$ ($\log \epsilon 2.65$).

*2-Benzyl-4,6-dimethoxycoumaran-3-one*¹ has $\lambda_{\text{max}} 283\text{ m}\mu$ ($\log \epsilon 4.29$), $315\text{ m}\mu$ (infl.) ($\log \epsilon 3.70$), $\lambda_{\text{min}} 246\text{ m}\mu$ ($\log \epsilon 3.01$).

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