The Chemistry of the Insoluble Red Woods. Part 13.[1] Synthesis of 2-(Flavan-3-yl)isoflav-3-enes and of 6-Benzyl-5-phenylbenzo[*a*]xanthens

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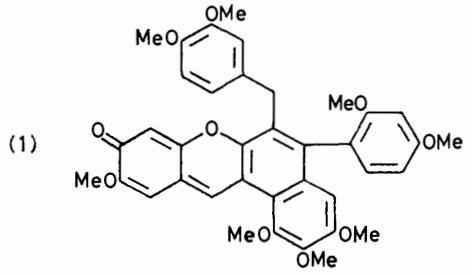
Methoxyisoflavylium perchlorates [type (4)] have been condensed with 3-(*o*-hydroxyphenyl)-1-phenylpropenes [type (5; R^1 = H)] to yield products which are formulated as 2-(flavan-3-yl)isoflav-3-enes [type (6)]. Condensation of the perchlorates (4) with 3-(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)propenes [type (5; R^1 = Me)] gave derivatives formulated as 6-benzyl-5-phenylbenzo[*a*]xanthens [type (3; R^5 = Me)], analogous to the xanthens formed from per-*O*-methylsantalin (1) and per-*O*-methylsantarubin (2) by reduction to the phenolic xanthen [type (3; R^5 = H)] and methylation.

THE permethyl ethers of the principal pigments, santalin and santarubin,[2] isolated from the 'insoluble red' woods, have structures (1) and (2) respectively.[3,4] Our hypothesis concerning the mode of biosynthesis of these pigments has received preliminary *in vitro* support.[1] In an extension of this putative biomimetic approach we have synthesised several 2-(flavan-3-yl)isoflav-3-enes



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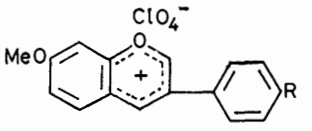

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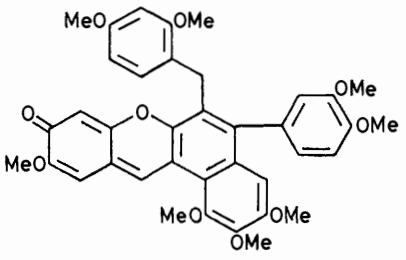

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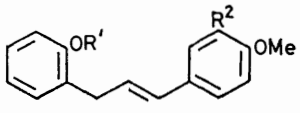

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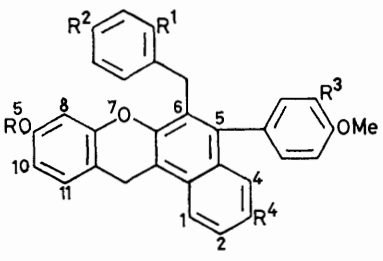

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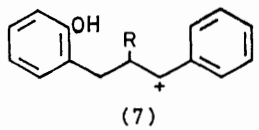

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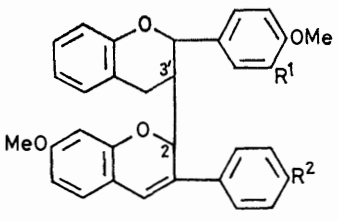

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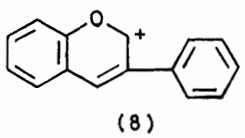


(8)

[type (6)] and a number of xanthens of type (3; R^5 = Me). This latter system is also produced by reduction

[1] Part 12, M. M. E. Badran and W. B. Whalley, *J.C.S. Perkin I*, 1976, 1389.

[2] A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 1954, 2794.

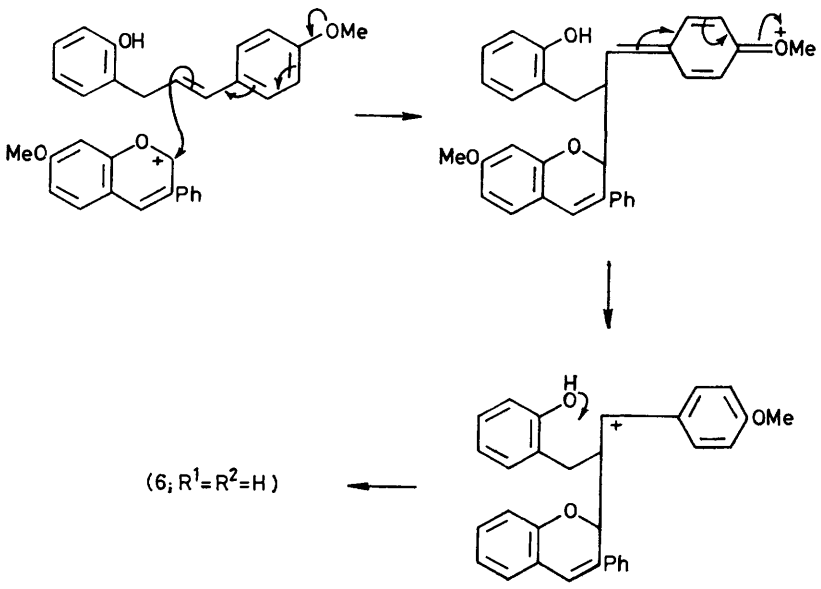
[3] D. W. Mathieson, B. J. Millard, J. W. Powell, and W. B. Whalley, *J.C.S. Perkin I*, 1973, 184.

[4] A. Arnone, L. Camarda, L. Merlini, and G. Nasini, *J.C.S. Perkin I*, 1975, 186.

of (1) and (2) to the phenolic xanthens [type (3; R^5 = H)] followed by methylation.[3]

The acid-catalysed condensation of 7-methoxyisoflavylium perchlorate (4; R = H) with the readily available [5] 3-(*o*-hydroxyphenyl)-1-(*p*-methoxyphenyl)-propene (5; $R^1 = R^2$ = H) occurred easily in aqueous methanol to yield a crystalline product devoid of hydroxy-groups and having spectral and analytical properties (see Table 1 and Experimental section) compatible with structure (6; $R^1 = R^2$ = H). This conclusion is in agreement with the genesis of (6; $R^1 = R^2$ = H) as shown in Scheme 1. This mechanism has its analogy in the conversion [5] of 3-(*o*-hydroxyphenyl)-1-(*p*-methoxyphenyl)prop-1-ene (5; $R^1 = R^2$ = H) into 4'-methoxyflavan under the influence of acid. In this analogy, protonation initiates cyclisation, presumably by way of the intermediate carbocation (7; R = H). In the pathway to (6; $R^1 = R^2$ = H), the carbocation (8), derived from the isoflavylium salt (4; R = H), functions as the electrophile to yield the intermediate ion [7; R = (8)].

Any possibility that our dimeric product was arising from the self-condensation of either compound (4; R = H) or (5; $R^1 = R^2$ = H) to form an isomer of (6; $R^1 = R^2$ = H) was excluded by (*a*) the condensation of 7-methoxyisoflavylium perchlorate (4; R = H) with 3-(*o*-hydroxyphenyl)-1-(3,4-dimethoxyphenyl)prop-1-ene (5; R^1 = H, R^2 = OMe) to yield (6; R^1 = OMe, R^2 = H), (*b*) the condensation of 4',7-dimethoxyisoflavylium perchlorate (4; R = OMe) with 3-(*o*-hydroxyphenyl)-1-(*p*-methoxyphenyl)prop-1-ene [5] (5; $R^1 = R^2$ = H) to yield (6; R^1 = H, R^2 = OMe), and (*c*) the fact that (6; R^1 = OMe, R^2 = H) and (6; R^1 = H, R^2 = OMe) each contained (n.m.r.) three methoxy-residues (Table 1) and had the requisite spectral characteristics. The mass spectra of these dimers were particularly characteristic. Thus, for example (6; $R^1 = R^2$ = H) furnished a molecular ion at *m/e* 476 (6.1%) together with ions at *m/e* 237 (100%) and 238 (20.7%) corresponding to structures (9) and (10), respectively. The other dimers of this group exhibited similar mass spectra. 'Blank' experiments established that neither the isoflavylium perchlorates nor the propenes yielded condensation products under the general reaction conditions. Further



SCHEME 1

TABLE 1

^{1}H N.m.r. data (τ values; 60 MHz) for compounds of type (6)

Compound:	(6; $R^1 = R^2$ = H)	(6; R^2 = H, R^1 = OMe)	(6; R^1 = H, R^2 = OMe)	(6; $R^1 = R^2$ = OMe)
ArH, H-4	2.85, 2.90—3.80 (17 H, m)	2.75, 2.85—3.50 (16 H, m)	2.80—3.59 (16 H, m)	2.82—3.61 (15 H, m)
H-2	4.35—4.40 (1 H, d, *J* 3.25 Hz)	4.32—4.42 (1 H, d, *J* 5.2 Hz)	4.30—4.35 (1 H, d, *J* 3.25 Hz)	4.46—4.50 (1 H, d, *J* 3.2 Hz)
H-2'	4.50—4.62 (1 H, d *J* 8.45 Hz)	4.55br (1 H, s)	4.50—4.65 (1 H, d, *J* 7.80 Hz)	4.60—4.70 (1 H, d, *J* 7.80 Hz)
OCH_3	6.25 (s), 6.35 (s) (6H)	6.18 (s), 6.35 (s) (9H)	6.20 (s), 6.21 (s), 6.29 (s) (9H)	6.30 (s), 6.50 (s) (12 H)
H-3'	7.20—7.40br (1 H, m)	7.20—7.40br (1 H, m)	7.10—7.40br (1 H, m)	7.20—7.50br (1 H, m)
H-4'	7.65br (2 H, m)	7.49br (2 H, m)	7.50br (2 H, m)	7.62br (2 H, m)

[5] M. M. Bokadia, B. R. Brown, D. Cobern, A. Roberts, and G. A. Somerfield, *J. Chem. Soc.*, 1962 1658.

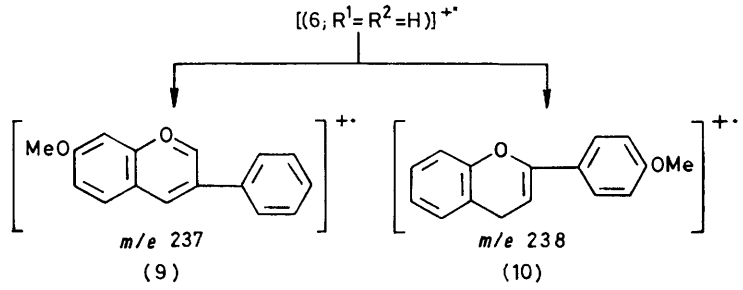
TABLE 2

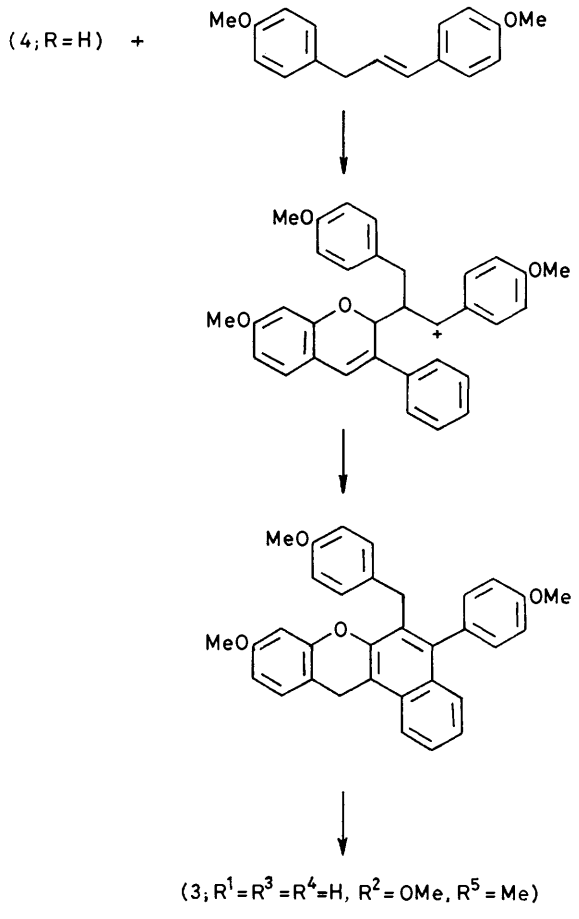
^{1}H N.m.r. data (τ values; 60 MHz) for compounds of type (3)

Compound	ArH	CH_2	*O*-Me
(3; $R^2 = R^4 = H$, $R^1 = R^3 = OMe$, $R^5 = Me$)	2.0—3.61 (14 H, m)	5.60 (s), 5.90 (s) (4 H)	6.09 (s), 6.25 (s), 6.27 (s), 6.50 (s) (12 H)
(3; $R^1 = R^3 = R^4 = H$, $R^2 = OMe$, $R^5 = Me$)	2.0—3.58 (15 H, m)	5.60 (s), 5.90 (s) (4H)	6.20 (s), 6.19 (s), 6.25 (s) (9H)
(3; $R^2 = H$, $R^1 = R^3 = R^4 = OMe$, $R^5 = Me$)	2.08 (s), 2.33 (s), 2.70—3.62 (m) (13 H)	5.68 (s), 5.95 (s) (4 H)	6.10 (s), 6.29 (s), 6.35 (s), 6.35 (s), 6.42 (s) (15 H)
(3; $R^1 = R^3 = H$, $R^2 = R^4 = OMe$, $R^5 = Me$)	2.08—3.43 (14 H, m)	5.63 (s), 5.96 (s) (4 H)	6.10 (s), 6.20 (s), 6.26 (s), 6.31 (s) 12 H)

indirect evidence for the mechanism of Scheme 1 was provided by the failure of attempts to condense isoflavylium perchlorates with 3-(*p*-hydroxyphenyl)-1-phenylpropenes. The structure of the propene (5; $R^1 = H$, $R^2 = OMe$) follows from (*a*) the method of preparation by analogy with (5; $R^1 = R^2 = H$), (*b*) the u.v. spectrum, and (*c*) the condensation with the isoflavylium salts to yield products directly analogous to those formed from (5; $R^1 = R^2 = H$).

We therefore investigated the reaction of isoflavylium perchlorates with 1,3-diarylpropenes devoid of hydroxy-residues, but containing electron-releasing methoxy-groups. Catalytic reduction of 4'-hydroxy-4-methoxychalcone furnished 1-(*p*-hydroxyphenyl)-3-(*p*-methoxyphenyl)propan-1-one, which was reduced by sodium borohydride to the corresponding alcohol. Dehydration of this formed the propene, which was methylated to give 1-(*p*-methoxyphenyl)-3-(*p*-methoxyphenyl)propene. Condensation of this propene with 7-methoxyisoflavylium perchlorate occurred rapidly in boiling acetonitrile to yield a product which on the basis of its spectral and analytical characteristics (Table 2 and Experimental section) is formulated as (3; $R^1 = R^3 = R^4 = H$, $R^2 = OMe$, $R^5 = Me$), and the genesis of which is probably as shown in Scheme 2.





SCHEME 2

Cognate xanthenes [type (3)] were similarly synthesised (i) from 4',7-dimethoxyisoflavylium perchlorate (4; R = OMe) and 3-(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)propene (5; $R^1 = Me$, $R^2 = H$), obtained by methylation of (5; $R^1 = R^2 = H$), (ii) from (4; R = OMe) and 3-(*o*-methoxyphenyl)-1-(3,4-dimethoxyphenyl)propene (5; $R^1 = Me$, $R^2 = OMe$), and (iii) from 7-methoxyisoflavylium perchlorate (4; R = H) and 3-(*o*-methoxyphenyl)-1-(3,4-dimethoxyphenyl)propene (5; $R^1 = Me$, $R^2 = OMe$).

Additional examples of the condensation of nitrogenous nucleophiles with isoflavylium perchlorates (*cf.* ref. 1) are recorded in the Experimental section.

EXPERIMENTAL

Reduction of Chalcones to Propenes.—The general method of Brown *et al.*[5] was used to prepare the following propenes from the corresponding chalcones.

(*a*) Methylation of 3-(*o*-hydroxyphenyl)-1-(*p*-methoxyphenyl)propene [5] (0.5 g) by acetone–methyl iodide–potassium carbonate gave 3-(*o*-*methoxyphenyl*)-1-(p-*methoxy*-

phenyl)propene (0.4 g), which formed needles, m.p. *ca.* 23°; τ 2.70—3.35 (8 H, m, ArH), 3.69—3.75 (2 H, t, C*H*=C*H*), 6.30 and 6.40 (6 H, s, OCH_3), and 6.49—6.55 (2 H, d, $ArCH_2$, *J* 5 Hz) (Found: M^+, 254.1311. $C_{17}H_{18}O_2$ requires *M*, 254.1307).

(*b*) 2′-Hydroxy-3,4-dimethoxychalcone (14.2 g) gave 1-(3,4-*dimethoxyphenyl*)-3-(o-*hydroxyphenyl*)*propene* (6 g) as needles, m.p. 127° [from benzene–light petroleum (b.p. 60—80 °C)]; $\nu_{max.}$ 3 440 cm^{-1} (OH); $\lambda_{max.}$ 218 (log ε 3.88) and 265 nm (3.69) (Found: C, 75.7; H, 6.8. $C_{17}H_{18}O_3$ requires C, 75.5; H, 6.7%).

1-(3,4-Dimethoxyphenyl)-3-(*o*-methoxyphenyl)propene formed an oil; τ 2.90—4.50 (7 H, m, ArH), 3.69—3.80 (2 H, t, CH=CH), 6.32 and 6.35 (9 H, s, OCH_3), and 6.49—5.08 (2 H, d, $ArCH_2$, *J* 5 Hz), M^+ 284.

Preparation of 1,3-*Diarylpropan*-1-*ones from Chalcones.—General method.* The chalcone (0.1 mol) dissolved in tetrahydrofuran (200 ml) was reduced over platinum oxide (0.5 g) during *ca.* 2½ h to give the propanone in more than 80% yield. The following propanones were thus prepared.

(a) 1-(p-*Hydroxyphenyl*)-3-*phenylpropan*-1-*one* separated from benzene–light petroleum (b.p. 60—80 °C) in plates, m.p. 104°; $\nu_{max.}$ 3 200 (OH) and 1 655 cm^{-1} (C=O) (Found: C, 80.1; H, 6.4. $C_{15}H_{14}O_2$ requires C, 79.7; H, 6.2%).

(b) 1-(p-*Hydroxyphenyl*)-3-(p-*methoxyphenyl*)*propan*-1-*one* formed needles, m.p. 122° [from benzene–light petroleum (b.p. 60—80 °C)]; $\nu_{max.}$ 3 180 (OH) and 1 650 cm^{-1} (C=O) (Found: C, 74.9; H, 6.5. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.3%).

(c) 3-(3,4-*Dimethoxyphenyl*)-1-(p-*hydroxyphenyl*)*propan*-1-*one* formed needles, m.p. 145° (from benzene); $\nu_{max.}$ 3 359 (OH) and 1 660 cm^{-1} (C=O) (Found: C, 71.1; H, 6.2. $C_{17}H_{18}O_4$ requires C, 71.3; H, 6.3%).

Prepared quantitatively in the normal manner the *acetate* formed plates, m.p. 50—51° (from ethanol); $\nu_{max.}$ 1 759 (acetate C=O) and 1 680 cm^{-1} (C=O) (Found: C, 70.0; H, 6.2. $C_{19}H_{20}O_5$ requires C, 69.5; H, 6.1%).

Preparation of 1,3-*Diarylpropan*-1-*ols from the Propan*-1-*ones.—General method.* A solution of the propan-1-one (0.025 mol) in methanol (60 ml) was reduced by addition of an excess of sodium borohydride at 60—65 °C. Next day the product (75% yield) was isolated.

(a) 1-(p-*Hydroxyphenyl*)-3-*phenylpropan*-1-*ol* formed prisms, m.p. 96—98° (from ethanol); $\nu_{max.}$ 3 310 cm^{-1} (OH) (Found: C, 79.1; H, 7.2. $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.1%).

(b) 1-(p-*Hydroxyphenyl*)-3-(p-*methoxyphenyl*)*propan*-1-*ol* separated from benzene–light petroleum (b.p. 60—80 °C) in prisms, m.p. 79—80°; $\nu_{max.}$ 3 395—3 140 cm^{-1} (OH) (Found: C, 74.5; H, 7.2. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%).

Conversion of 1,3-*Diarylpropan*-1-*ols into* 1,3-*Diarylpropenes.—General method.* A solution of 1-(*p*-hydroxyphenyl)-3-phenylpropan-1-ol (1.52 g) in toluene (30 ml) containing anhydrous oxalic acid (4 g) was refluxed for 4 h; the product was then isolated. 1-(p-*Hydroxyphenyl*)-3-*phenylpropene* formed needles, m.p. 84—85° [from benzene–light petroleum (b.p. 40—60 °C)]; $\nu_{max.}$ 3 340 cm^{-1} (OH); τ 2.80 (5 H, s, ArH), 2.85—2.29 (2 H, m, ArH), 3.25—3.49 (2 H, m, ArH), 3.72—3.86 (2 H, d, CH=CH), 4.75 (1 H, s, OH, replaceable with D_2O), and 6.49—6.58 (2 H, d, $ArCH_2$, *J* 6.5 Hz) (Found: C, 85.8; H, 6.8. $C_{15}H_{14}O$ requires C, 85.7; H, 6.7%).

Prepared similarly, 1-(p-*hydroxyphenyl*)-3-(p-*methoxyphenyl*)*propene* formed plates, m.p. 90—92° [from benzene–light petroleum (b.p. 60—80 °C)]; $\nu_{max.}$ 3 420 cm^{-1} (OH); $\lambda_{max.}$ 210 (log ε 3.70) and 262 nm (3.69); τ 2.65—3.35 (8 H, m, ArH), 3.70—3.85 (2 H, d, CH=CH, *J* 6 Hz), 4.50—4.80 (1 H, s, OH, replaceable with D_2O), 6.02 (3 H, s, OCH_3), and 6.47—6.58 (2 H, d, $ArCH_2$, *J* 6.5 Hz) (Found: C, 80.3; H, 6.7. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7%).

1,3-*Bis*-(p-*methoxyphenyl*)*propene*, prepared by methylation of the foregoing phenol, formed plates, m.p. 59—60° [from benzene–light petroleum (b.p. 40—60 °C)] (Found: C, 80.0; H, 7.1. $C_{17}H_{18}O_2$ requires C, 80.3; H, 7.1%).

Condensation of Isoflavylium Perchlorates with 3-(o-*Hydroxyphenyl*)-1-*phenylpropenes.*—(*a*) 7-Methoxyisoflavylium perchlorate (0.17 g) was added to a solution of 3-(*o*-hydroxyphenyl)-1-(*p*-methoxyphenyl)propene (0.12 g) in 1% hydrochloric acid–methanol (5 ml) at 50—60 °C. The pink solution rapidly became colourless and a crystalline solid separated during 14 h at room temperature. Purification from methanol gave 2-(4-*methoxyflavan*-3-*yl*)-7-*methoxyisoflav*-3-*ene* (6; R^1 = R^2 = H) in needles, m.p. 167—168°; $\lambda_{max.}$ 243 (log ε 3.75), 282 (3.53), and 330 nm (3.54) (Found: C, 81.1; H, 6.0%; M^+, 476.2016. $C_{32}H_{28}O_4$ requires C, 80.7; H, 5.9%; *M*, 476.1989).

(*b*) Similarly, condensation of 7-methoxyisoflavylium perchlorate (0.34 g) and 3-(*o*-hydroxyphenyl)-1-(3,4-dimethoxyphenyl)propene (0.27 g) gave 2-(3,4-*dimethoxyflavan*-3-*yl*)-7-*methoxyisoflav*-3-*ene* (6; R^2 = H, R^1 = OMe) in fluffy needles (0.4 g), m.p. 152—154° (from methanol); $\lambda_{max.}$ 245 (log ε 3.76), 285 (3.46), and 330 nm (3.68) (Found: C, 78.2; H, 6.0%; M^+, 506.2084. $C_{33}H_{30}O_5$ requires C, 78.2; H, 6.0%; *M*, 506.2092).

(*c*) Likewise condensation of 4′,7-dimethoxyisoflavylium perchlorate (0.37 g) with 3-(*o*-hydroxyphenyl)-1-(*p*-methoxyphenyl)propene (0.25 g) gave 4′,7-*dimethoxy*-2-(4-*methoxyflavan*-3-*yl*)*isoflav*-3-*ene* (6; R^1 = H, R^2 = OMe) (0.3 g), which formed needles, m.p. 140° (from methanol–acetone); $\lambda_{max.}$ 243 (log ε 3.64), 280 (3.50), and 327 nm (3.27) (Found: C, 77.9; H, 5.9%; M^+, 506.2078. $C_{33}H_{30}O_5$ requires C, 78.2; H, 6.0%; *M*, 506.2093).

(*d*) Condensation of 4′,7-dimethoxyisoflavylium perchlorate (0.37 g) with 1-(3,4-dimethoxyphenyl)-3-(*o*-hydroxyphenyl)propene (0.27 g) gave 2-(3,4-*dimethoxyflavan*-3-*yl*)-4′,7-*dimethoxyisoflav*-3-*ene* (6; R^1 = R^2 = OMe) (0.35 g) in needles, m.p. 186—187° (from acetone–methanol); $\lambda_{max.}$ 240 (log ε 3.94), 272 (3.80), and 322 nm (3.27) (Found: C, 76.0; H, 6.0%; M^+, 536.2220. $C_{34}H_{32}O_6$ requires C, 76.1; H, 6.0%; *M*, 536.2200).

Condensation of Isoflavylium Perchlorate with 1,3-*Diarylpropenes.*—(*a*) A solution of 7-methoxyisoflavylium perchlorate (0.68 g) and 1-(3,4-dimethoxyphenyl)-3-(*o*-methoxyphenyl)propene (0.56 g) in acetonitrile (20 ml) was refluxed for 3 h. Sodium borohydride was added to the cooled solution to discharge residual colour and the product was isolated. Chromatography on alumina from light petroleum (b.p. 60—80 °C)–benzene (3 : 1) gave (i) 7-methoxyisoflav-3-ene (0.1 g), identical with an authentic specimen, and (ii) 5-(3,4-*dimethoxyphenyl*)-9-*methoxy*-6-(2-*methoxybenzyl*)*benzo*[a]*xanthen* (3; R^1 = R^3 = OMe, R^2 = R^4 = H, R^5 = Me) (0.15 g), which separated from acetone–methanol in very pale yellow needles, m.p. 186—187°; $\lambda_{max.}$ 240 (log ε 3.80), 249infl (3.86), 275infl (3.55), and 328 nm (2.71) (Found: C, 77.6; H, 5.7%; M^+, 518.2099. $C_{34}H_{30}O_5$ requires C, 78.7; H, 5.8%; *M*, 518.2094).

(*b*) 7-Methoxyisoflavylium perchlorate (0.6 g) and 1,3-bis-(*p*-methoxyphenyl)propene (0.45 g) gave 9-*methoxy*-6-(4-*methoxybenzyl*)-5-(4-*methoxyphenyl*)*benzo*[a]*xanthen* (3;

$R^1 = R^3 = R^4 = H$, $R^2 = OMe$, $R^5 = Me$) (0.21 g), which formed sandy coloured prisms, m.p. 173—174° (from methanol–acetone); $\lambda_{max.}$ 258 (log ε 4.07), 288infl (3.62), and 330 nm (2.93) (Found: C, 79.5; H, 5.8%; M^+, 488.1996. $C_{33}H_{28}O_4$ requires C, 81.1; H, 5.8%; *M*, 488.1988).

(*c*) Prepared from 4′,7-dimethoxyisoflavylium perchlorate (0.66 g) and 1-(3,4-dimethoxyphenyl)-3-(*o*-methoxyphenyl)-propene (0.5 g), 5-(3,4-*dimethoxyphenyl*)-3,9-*dimethoxy*-6-(2-*methoxybenzyl*)*benzo*[a]*xanthen* (3; $R^2 = H$, $R^1 = R^3 = R^4 = OMe$, $R^5 = Me$) (0.21 g) formed needles, m.p. 208—210° (from methanol–acetone); $\lambda_{max.}$ 256 (log ε 4.70), 283infl (3.80), 291infl (3.72), and 355 nm (3.14) (Found: C, 76.1; H, 5.6%; M^+, 548.2197. $C_{35}H_{32}O_6$ requires C, 76.6; H, 5.9%; *M*, 548.2199).

(*d*) 4′,7-Dimethoxyisoflavylium perchlorate (0.5 g) and 1,3-bis-(*p*-methoxyphenyl)propene (0.38 g) gave 3,9-*dimethoxy*-6-(4-*methoxybenzyl*)-5-(4-*methoxyphenyl*)*benzo*[a]-*xanthen* (3; $R^1 = R^3 = H$, $R^2 = R^4 = OMe$, $R^5 = Me$) (0.1 g) in pale yellow needles, m.p. 172—173°; $\lambda_{max.}$ 260 (log ε 4.08), 290infl (3.68), and 350 nm (3.07) (Found: C, 77.8; H, 5.7%; M^+, 518.2101. $C_{34}H_{30}O_5$ requires C, 78.7; H, 5.8%; *M*, 518.2094).

Derivatives of 7-Methoxyisoflavylium Perchlorate.—Prepared from aniline (0.1 g) and the perchlorate (0.3 g) 2-p-*aminophenyl*-7-*methoxyisoflav*-3-*ene* (0.2 g) formed stout yellow needles, m.p. 102°; $\lambda_{max.}$ 247 (log ε 3.71) and 337 nm (3.58) (Found: C, 80.2; H, 5.9; N, 4.4. $C_{22}H_{19}NO_2$ requires C, 80.2; H, 5.8; N, 4.3%).

Prepared from di-isopropylamine, 2-(*di-isopropylamino*)-7-*methoxyisoflav*-3-*ene* formed prisms, m.p. 143°; $\lambda_{max.}$ 246 (log ε 3.85) and 325 nm (3.56); τ 2.30—2.72, 2.85—3.05, and 3.32—3.75 (8 H, m, ArH, H-4 ,and H-2), 6.18 (3 H, s, OCH_3), 6.45—6.90 (2 H, m, 2 tert. H), 8.90—9.0 (12 H, d, *J* 6.5 Hz, 4 × NCH_3) (Found: C, 78.1; H, 7.8; N, 3.9. $C_{22}H_{27}NO_2$ requires C, 78.3; H, 8.1; N, 4.2%).

Prepared from 7-methoxyisoflavylium perchlorate (0.4 g) and *p*-dimethylaminocinnamic acid (0.2 g) in refluxing acetic acid (20 ml) during 15 min, 2-p-*dimethylaminostyryl*-7-*methoxyisoflav*-3-*ene* (0.2 g) formed prisms, m.p. 126° (from methanol); τ 2.62—2.99 (12 H, m, ArH), 3.05—3.58 (2 H, m, CH=CH), 3.85 (1 H, s, OCH–), 6.25 (3 H, s, OCH_3), 7.10 (6 H, s, 2 × NCH_3), and 5.95 (1 H, s, ArCH) (Found: C, 82.0; H, 6.8; N, 3.8. $C_{26}H_{25}NO_2$ requires C, 81.5; H, 6.6; N, 3.7%).

Derivatives of 4′,7-Dimethoxyisoflavylium Perchlorate.—2-p-*Aminophenyl*-4′,7-*dimethoxyisoflav*-3-*ene* formed needles, m.p. 124° (from methanol); $\lambda_{max.}$ 242 (log ε 3.67) and 328 nm (3.81) (Found: C, 76.3; H, 5.9; N, 5.0. $C_{23}H_{21}NO_3$ requires C, 76.9; H, 5.9; N, 4.0%).

2-(*Di-isopropylamino*)-4′,7-*dimethoxyisoflav*-3-*ene* formed long needles, m.p. 115° (from methanol); $\lambda_{max.}$ 245 (log ε 3.58) and 328 nm (3.71); τ 2.45—3.85 (9 H, m, ArH), 6.25 and 6.27 (6 H, s, 2 × OCH_3), 6.50—6.95 (2 H, m, tert. CH), and 8.98—9.08 (12 H, d, *J* 6.5 Hz, 4 × NCH_3) (Found: C, 74.6; H, 7.6; N, 3.6. $C_{23}H_{29}NO_3$ requires C, 75.2; H, 8.0; N, 3.8%).

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