Some Novel Photochemical and Related Aryl Couplings and Migrations in Flavonoid Synthesis

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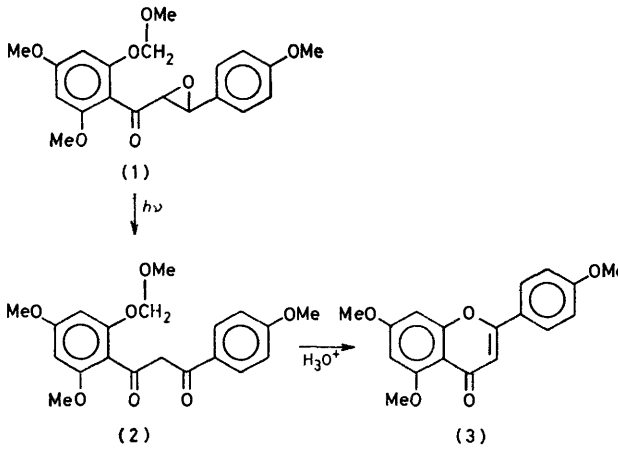
2'-Methoxymethoxy-4,4',6'-trimethoxychalcone epoxide couples at the β-position with 3,5-dimethoxyphenol under photolytic conditions to form isomeric 1,3,3-triaryl-2-hydroxypropiophenones. These propiophenones are subject to photo-induced α-ketol rearrangements yielding isomeric 1-hydroxypropan-2-ones. Together these serve as useful synthetic intermediates for 4-arylflavan-3-ones and novel 2-hydroxy-2-arylbenzylbenzo[*b*]furan-3(2*H*)-ones and 4-aryl-3-hydroxy-3,4-*cis*-dihydrocoumarins. The same epoxide reacts ionically under ambient conditions with 2,4,6-trihydroxybenzoic acid to afford a 3-*O*-benzoylpropiophenone intermediate, which provides novel access to isoflavones in high overall yield. Analogous coupling of phloroglucinol to epoxycinnamates gives diastereoisomeric 3,3-diaryl-2-hydroxypropionates which serve as precursors for 3,4-*trans*- and 3,4-*cis*-4-aryl-3-hydroxydihydrocoumarins and thence for 3-aryl- and 3-hydroxycoumarins.

CARBON–carbon coupling of phenolic units to the α-position of chalcones as primary step in our attempted synthesis of 2(3),7-linked biflavonoids[1-4] under oxidative conditions [alkaline $K_3Fe(CN)_6$;[5] alkaline H_2O_2[6]] invariably led to intermolecular β-coupling. However, the facile photolytic conversion of the readily accessible *O*-alkylated αβ-epoxychalcones to β-diketones[7] *via* C_α–O fragmentation of the oxiran moiety offered the best alternative route for effecting the desired α-coupling.

Thus, irradiation of the stable 4,4',6'-trimethoxy-2'-methoxymethoxy-*trans*-chalcone epoxide (1)[6] in benzene

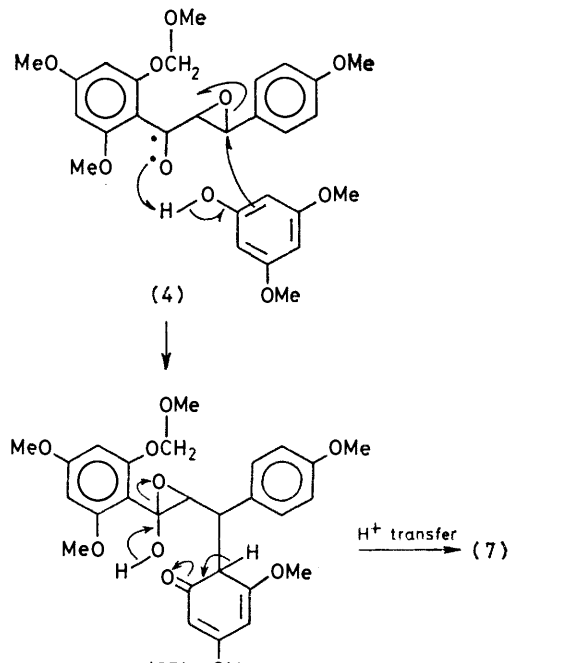


(1) (2) (3)

gives the anticipated heterolytic C_α–O fragmentation and hydrogen transfer to form the β-diketone (2). Structural proof of the latter is provided by its acid-catalysed cyclization to 4',5,7-trimethoxyflavone (3).

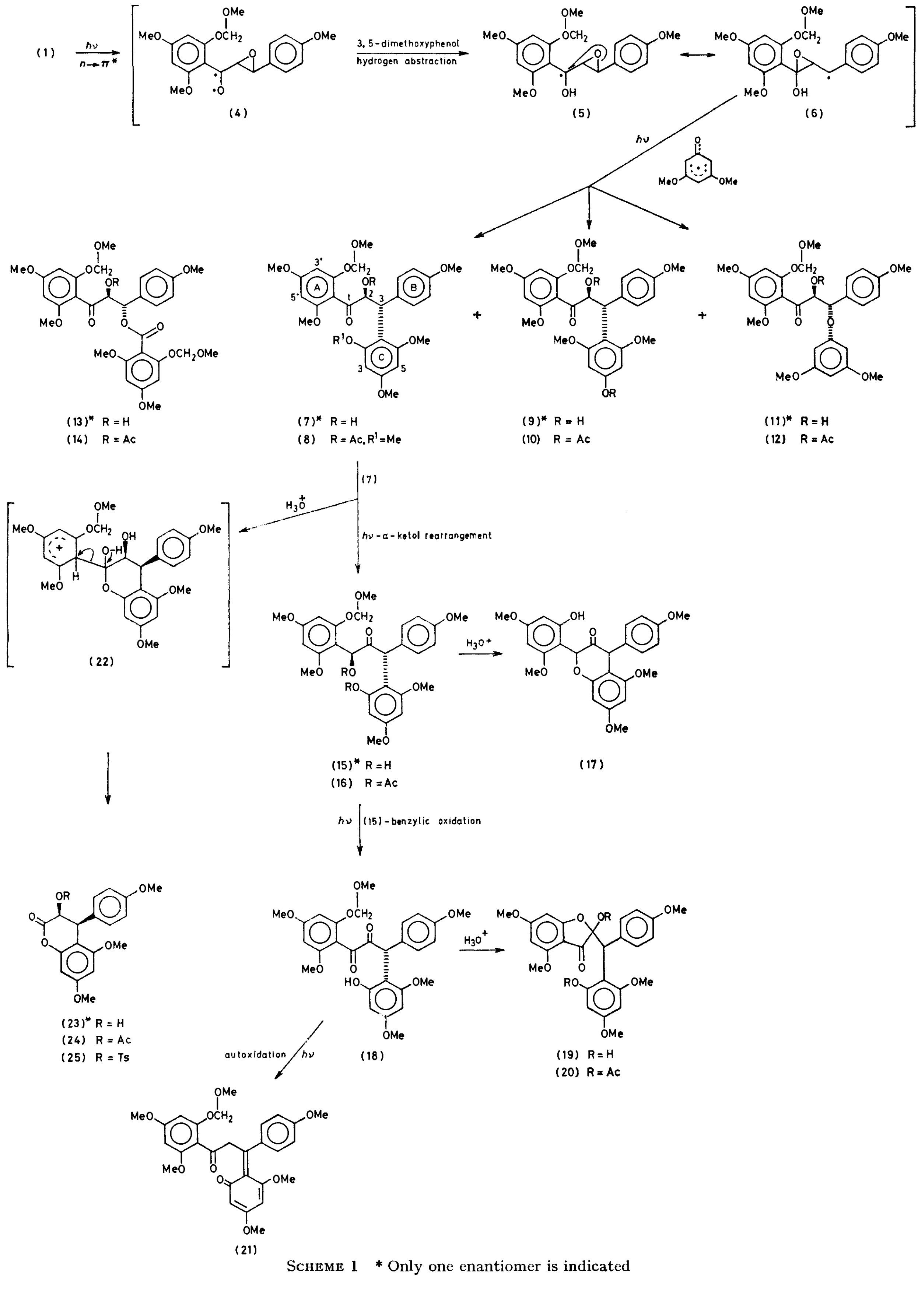
Photolysis of the same epoxide (1) under identical conditions except for the presence of 3,5-dimethoxyphenol leads to a complex mixture (47% overall yield) of products which could be divided into three categories, *i.e.* C_β–C coupled analogues (7), (9), (15), (18), and (21), a C_β–O coupled isomer (11), and a C_β–O linked ester (13) (Scheme 1).

C_β–C *Coupled* 3-*Arylpropiophenones and their Chemical Conversions*.—The novel photochemical aryl couplings leading to the isomeric 1,3,3-triaryl-2-hydroxypropiophenones (7) and (9) are presumed to occur mechanistically *via* hydrogen abstraction from 3,5-dimethoxyphenol by the excited *n*,π*-carbonyl group (4). Rearrangement of the benzylic radical (5) to the isomeric hemiacetal equivalent (6) followed by combination with the phenoxyl radical leads to single racemates for each of the propiophenones (7) and (9), the latter being available in pure form only as the diacetate (10). The low yield (*ca.* 2%) of the 3-(4-hydroxy-2,6-dimethoxyphenyl) isomer (9) contrasts with its formation as the major product under ionic conditions.[6] This may reflect either a concerted type of mechanism [(4) ⟶ (37) ⟶ (7)] or increased

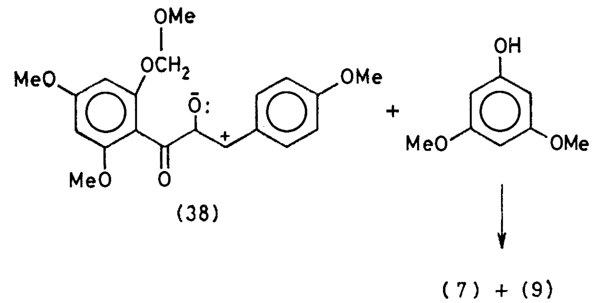


(4) (37)

steric hindrance at the 4-position of 3,5-dimethoxyphenol relative to C-2, both factors favouring formation of the 3-(2-hydroxy-4,6-dimethoxyphenyl)analogue (7). Since homolysis of the C_β–O bond of the oxiran moiety in epoxide (1) results in the formation of dissimilar radical centres which may degenerate to a zwitterionic intermediate (38), ionic formation of propiophenones (7)

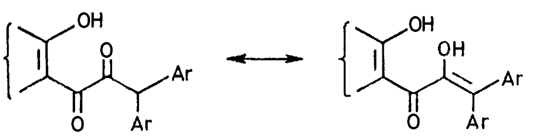


SCHEME 1 * Only one enantiomer is indicated and (9) represents a plausible alternative to the proposed radical pathways.



Propiophenone (7) presumably serves as the precursor to the isomeric 1,3,3-triaryl-1-hydroxypropan-2-one (15) *via* α-ketol rearrangement by means of photo-enolization.[8] Subsequent benzylic autoxidation of the propan-2-one (15) results in the formation of the oxygen-labile α-diketone (18) which is converted to the stable quinone methide (21) by further autoxidation.[9] The C_β–C linked compounds (7), (9), (15), (18), and (21) represent the 3-(4-methoxyphenyl) analogues of those previously obtained by epoxide-mediated stereoselective β-coupling of 3,5-dimethoxyphenol to 2′-methoxymethoxy-4-hydroxychalcones [6,9] and were accordingly identified by means of n.m.r. and mass spectrometric comparison.

Considering the continuing controversy regarding the factors governing the cyclization of chalcones in general,[10] the propiophenone (7) (equivalent of a β-aryl-α-hydroxydihydrochalcone), the α-diketone (18) (keto-form of a β-aryl-α-hydroxychalcone analogue), and the structurally related propan-2-one (15), which have in common competitive nucleophilic functionality on the β-aryl moiety, all offer opportunity for extending existing parameters regulating such cyclizations under acid conditions. Thus, whereas acid-induced cyclization of the 1-hydroxypropan-2-one (15) to the 4-arylflavan-3-one (17) *via* the ring C hydroxy and the incipient benzylic carbocation (destabilised by adjacent carbonyl) takes precedence over the presumed competitive ring A hydroxy and protonated carbonyl pathway, alternative formation of the five-membered heterocycle in the 2-(α-arylbenzyl)-2-hydroxybenzo[*b*]furan-3(2*H*)-one (19) from the α-diketone is strongly favoured by protonation of the enolic double bond in (39) and the subsequent



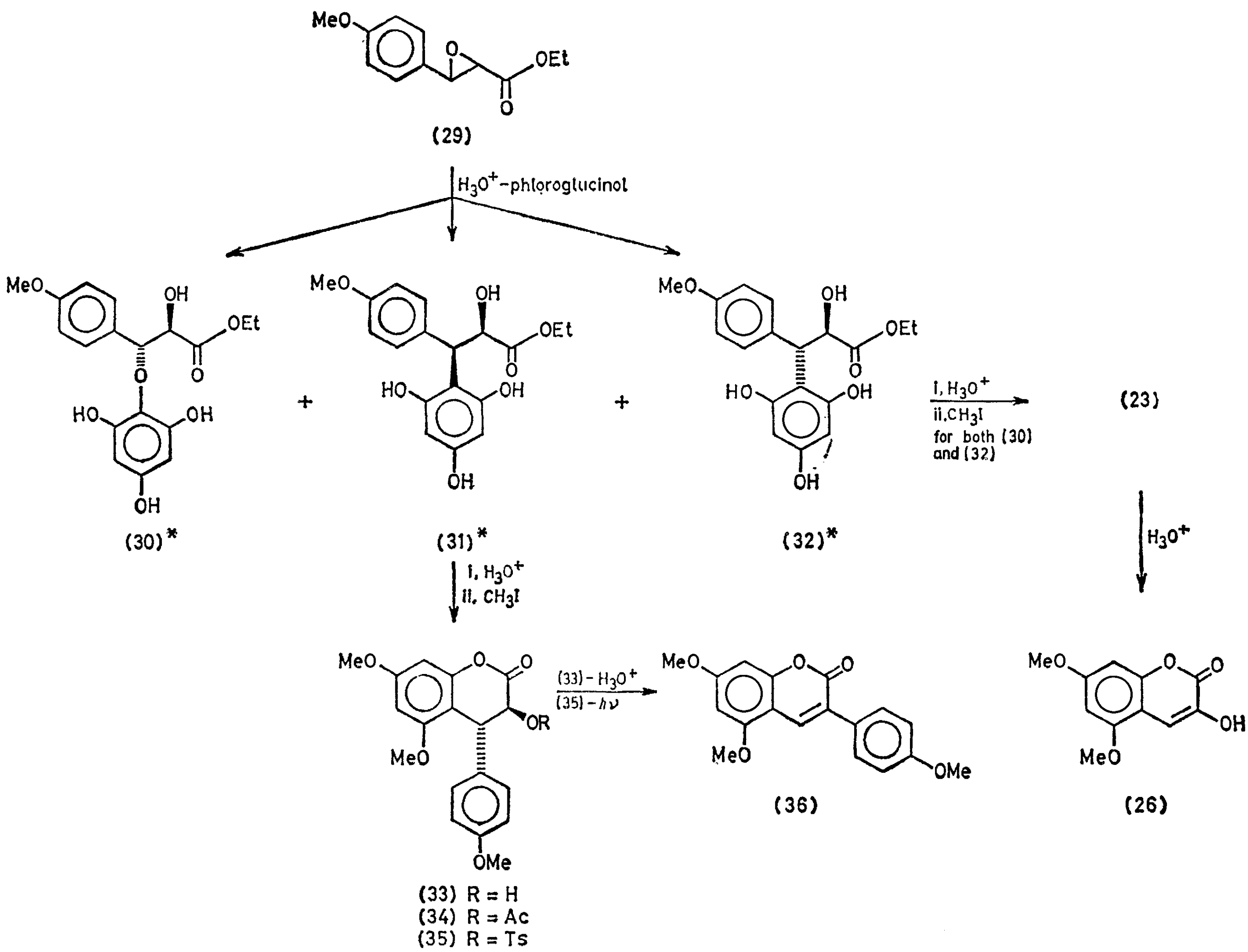
combined inductive effects of the carbonyl and α-hydroxy-functions as was previously demonstrated by us.[10] Similar treatment of the propiophenone (7), where the potential for cyclization is obviously restricted to the ring C hydroxy and the carbonyl group, results in racemic 4-aryl-3-hydroxy-3,4-*cis*-dihydrocoumarin (23). Formation of the latter may be rationalized by invoking an intermediate protonated hemiacetal (22) which is subsequently transformed into the dihydrocoumarin (23) by concerted loss of the hydroxy proton and heterolytic fission of carbon–carbon linkage. This interesting C–C bond ' hydrolysis ' bears some resemblance to the rupture of interflavonoid carbon–carbon bonds of polyflavonoids (tannins) with consequent formation of anthocyanidins, as well as to acid-catalysed toluene-α-thiol fission of polyleucocyanidins.[11] Since n.m.r. data do not permit stereochemical assignment of the dihydrocoumarin (23) [chemical shifts of H-3 and H-4 coincide, δ 4.77, broad singlet for the free phenol (23), $J_{3,4}$ 7.0 Hz for the acetate (24)] confirmation of structure (23) was sought by synthesis (Scheme 2).

Mild acid treatment (0.1M-HOAc) of the epoxycinnamate (29) (Scheme 2), obtained by Darzen's condensation of 4-methoxybenzaldehyde with chloroethyl acetate,[12] with phloroglucinol gives besides the C_β–O coupled ester (30) (6.9%), also two diastereomeric C_β–C linked esters (31) and (32) both in low yield (6.3 and 7.5%, respectively). Under more strongly acidic conditions (0.05M-H_2SO_4) these esters (31) and (32) are individually converted after methylation into the respective 4-aryl-3-hydroxy-3,4-*trans*- (33) and -3,4-*cis*-dihydrocoumarins (23) [$J_{3,4}$ 6.8 and 2.7 Hz for (23) and (33), respectively]. However, coupling of phloroglucinol to the epoxycinnamate (29) in 0.05M-H_2SO_4 solution gives after methylation the dihydrocoumarins (23) and (33) directly, both in considerably higher yield. When treated with acid these diastereoisomers exhibit marked selectivity in the reaction course which enables unequivocal assignment of their 3,4-stereochemistry.

Individual acid treatment of the dihydrocoumarins (23) and (33) lead to the selective generation of the 3-hydroxycoumarin (26) and 3-arylcoumarin (36), respectively. A *trans*-diaxial orientation of the 3-hydroxy- and 4-aryl groups and thus a 3,4-*trans*-configuration of the dihydrocoumarin (33) is a prerequisite for formation of the 3-arylcoumarin (36) since the required formal dehydration *via* an incipient carbocation α to the lactone carbonyl (unfavourable) may then be enhanced by anchimeric π-bond assistance. Subsequent rearrangement of the intermediate benzenonium species (40) by concerted deprotonation and 1,2-aryl shift gives the 3-arylcoumarin (36). The low-field position of 4-H (δ 8.05) in the n.m.r. spectrum of (36) differentiates it from the isomeric 4-aryl derivative (42) (δ 5.87) obtained synthetically.[13] The remaining dihydrocoumarin (23) where *anti*-elimination of the 4-methoxyaryl- and 3-H *via* protonated species (41) takes precedence over dehydration, therefore, possesses 3,4-*cis*-stereochemistry.

Acid treatment (0.05M-H_2SO_4) of the C_β–O linked ester (30) followed by methylation also gives the 3,4-*cis*-dihydrocoumarin (23). This result may be explained in terms of the facile heterolysis of the protonated benzylic C_β–O bond assisted by participation of the neighbouring *anti*-hydroxy-group (43). Re-coupling of the liberated phloroglucinol *via* the protonated epoxide (44) gives the C_β–C coupled ester (32) which is subsequently cyclized to the 3,4-*cis*-analogue (23).

The 4-aryl-3-hydroxydihydrocoumarin pair (23) and (33) could serve, *via* the equivalent of dehydration, as useful precursors to the 4-arylcoumarin class of neoflavonoids. Photolysis of the 3,4-*trans*-3-*O*-tosyl derivative (35), however, gives a high-yield conversion (79%) to the 3-arylcoumarin (36). Under similar conditions both the 3,4-*cis*-derivative (25) and the 4-aryl-3-hydroxydihydrocoumarins (23) and (33) are stable, the former giving trace quantities of the same coumarin (36) only after prolonged reaction time. These results indicate that the course of the photolytic reaction, *i.e.* heterolytic cleavage of the 3-tosyloxy bond *via* the benzenonium species (40) is controlled by the same stereoelectronic factors as indicated for the acid-catalysed conversions.

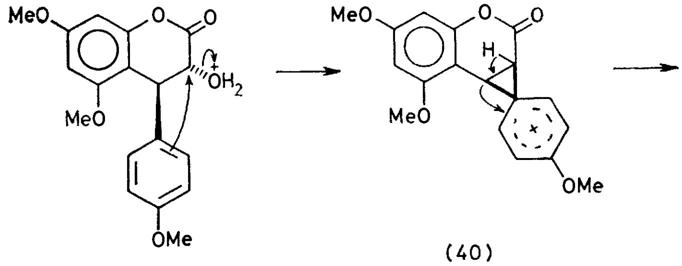


SCHEME 2 * Only one enantiomer is indicated

C_β–O *Coupled* 3-*Arylpropiophenone* (11).—The C_β–O linked analogue (11) (Scheme 1) presumably originates photochemically from the same free-radical pathway as was postulated for the C_β–C coupled isomers (7) and (9) except for coupling through the oxygen function of 3,5-dimethoxyphenol. Formation of a monoacetate (12) on acetylation and the appearance of the ring C aromatic protons as a three-proton multiplet (δ 5.85) in comparison with one-proton doublets (δ 5.69 and 5.30; *J* 2.0 Hz) in the n.m.r. spectrum of the isomeric propiophenone (7) differentiate between the two classes of propiophenones.

C_β–O *Linked Ester* (13), *its Origin, and Chemical Conversion*.—Since, in the absence of irradiation, spontaneous reaction of the epoxide (1) with 2,4,6-trihydroxybenzoic acid at ambient temperatures affords a 3-*O*-benzoylpropiophenone (45) analogue, the related step in the formation of the β-ester (13) during photolysis does not involve a quantum process. Under the latter conditions nucleophilic attack by 2-methoxymethoxy-4,6-dimethoxybenzoic acid [obviously generated by photolytic α-fission of the epoxide (1)[14]], therefore, gives the 3-*O*-benzoyl-2-hydroxypropiophenone (13).

However, this β-ester on acid hydrolysis gives both the expected 2,3-*trans*-3-hydroxyflavanone (28) (32%) and the isoflavone (27) (50%), while under anhydrous conditions the latter represents the sole product. Formation of the isoflavone is remarkable considering that racemic 2,3-*trans*-3-hydroxyflavanone cannot function as an intermediate as it is not convertible into the isoflavone even under drastic conditions. Formation of the isoflavone from the β-ester is accordingly rationalized by a 1,2-aroyl O ⟶ O shift[15] to the α-ester (49) followed by rearrangement of the resultant 3-*O*-benzoyldihydroflavonol intermediate (50) (*cf.* Scheme 3). Considering the mild conditions required for the conversion [(1) ⟶ (47) ⟶ (27)], this new high yield method may usefully complement existing isoflavonoid syntheses.[16]



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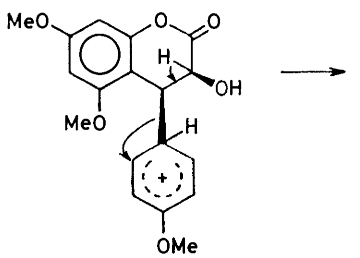

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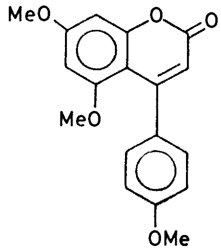

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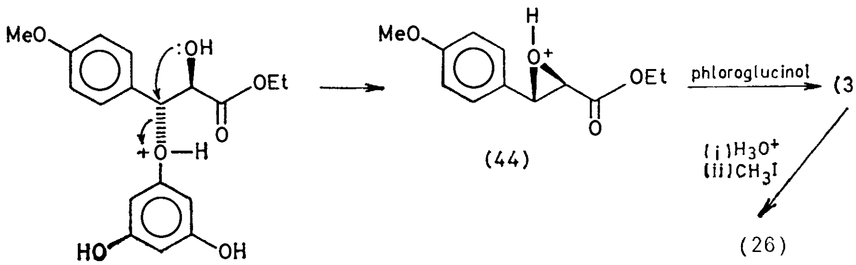
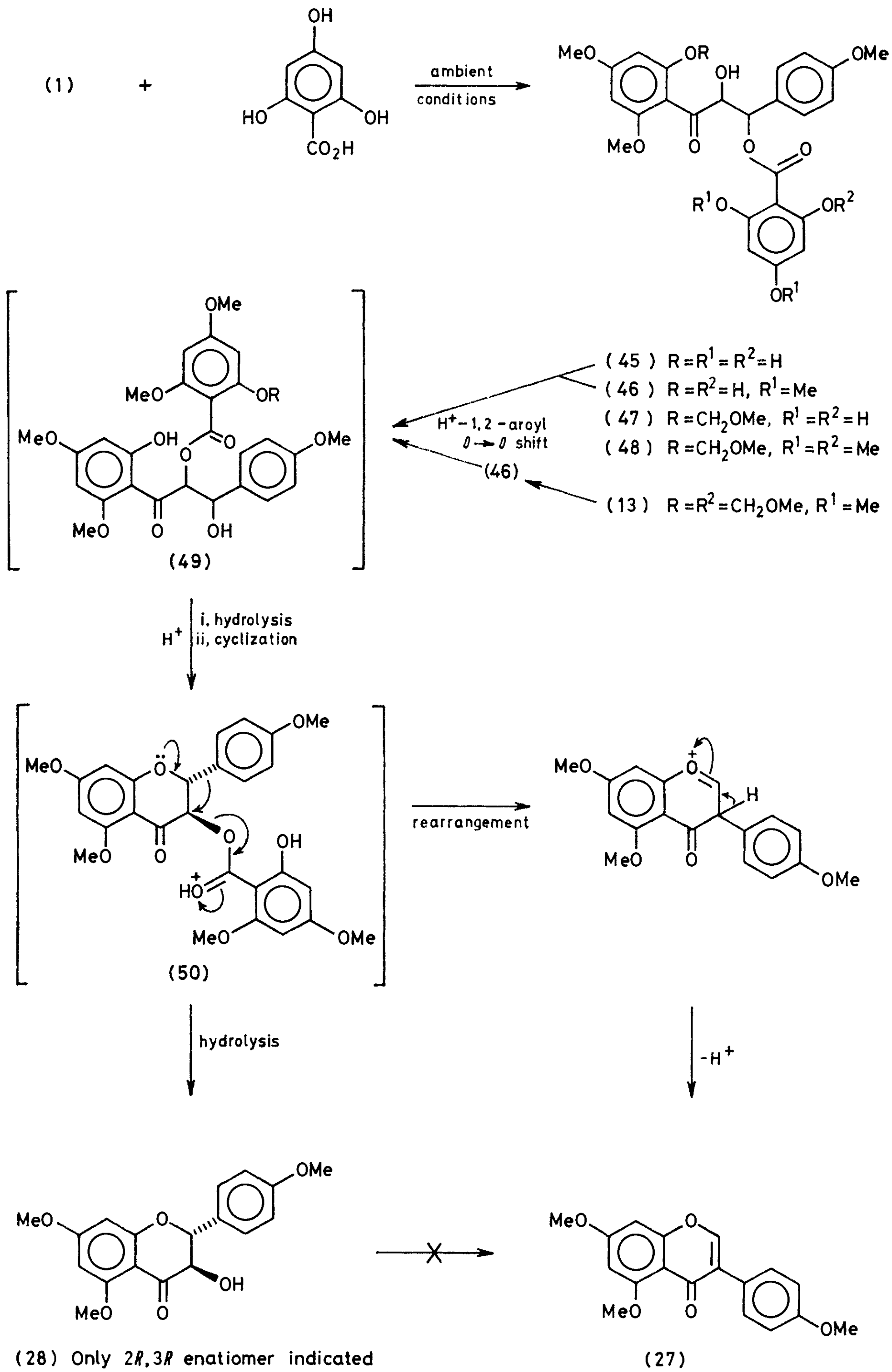


(43) (44) (32) (26)

EXPERIMENTAL

Irradiation of compounds in benzene in a quartz vessel was carried out in a Rayonet photochemical reactor at 250 nm and under a slow current of nitrogen (*ca.* 1 ml min^{-1}) unless otherwise specified. T.l.c. was performed on DC-Plastikfolien Kieselgel $60F_{254}$ (0.25 mm) and the plates sprayed with H_2SO_4–HCHO (40 : 1) after development. Colours indicated are those obtained with this reagent. Preparative plates [Kieselgel PF_{254} (1.0 mm)] were air-dried and used without prior activation. Column chromatography was performed on Kieselgel 60 (230—400 mesh; Merck). Methylations were performed either with an excess of diazomethane in methanol–diethyl ether at −15 °C for 48 h or with methyl iodide in anhydrous acetone–K_2CO_3 under reflux at 60 °C, while acetylations were carried out with acetic anhydride–pyridine. M.p.s were determined with a Reichert hot-stage apparatus and are uncorrected. ^{1}H N.m.r. spectra were recorded on a Bruker WP-80 spectrometer in $CDCl_3$ solutions (unless stated otherwise) with Me_4Si as internal standard, mass spectral data on a Varian CH-5 instrument, and i.r. data on a Unicam SP 1000 spectrophotometer for solutions in $CHCl_3$ (unless stated otherwise). Analyses (C and H) were performed by Analytische Laboratorien, Elbach, Germany.

Photolysis of 4,4′,6′-*Trimethoxy*-2′-*methoxymethoxy*-trans-*chalcone Epoxide* (1).—The chalcone epoxide (500 mg)[6] in benzene (50 ml) was irradiated for 0.5 h, the solvent evaporated, and the mixture separated by p.l.c. with benzene–acetone (9 : 1). The R_F 0.60 fraction (160 mg; light yellow) afforded the β-*diketone* (2) as an amorphous pale red solid, *m/e* 374 (M^+, 10.5%), 343 (39), 313 (70), 239 (6.3), 225 (47), 149 (16.7), and 135 (100); δ 7.90 (d, 2- + 6-H, *J* 8.5 Hz), 6.91 (d, 3- + 5-H, *J* 8.5 Hz), 6.37, 6.21 (dd, 3′- +



SCHEME 3

5′-H, *J* 2.0 Hz), 6.37 (s, enolic OH), 5.15 (s, CH_2), 3.84 (9 H), and 3.48 (s, 4 × OMe); $\nu_{max.}$ 1 612 cm^{-1} (Found: M^+, 374.133. $C_{20}H_{22}O_7$ requires *M*, 374.137).

The β-diketone (160 mg) in methanol (45 ml) was refluxed for 1 h with 1.5M-H_2SO_4 (2 ml). The mixture was diluted with water (250 ml) and extracted with ether (3 × 50 ml). Evaporation of the solvent followed by crystallization from methanol gave 4′,5,7-trimethoxyflavone (3) (95 mg) as needles, m.p. 156—157° (lit.,[17] 156°).

Photolysis of the Chalcone Epoxide (1) *in the Presence of* 3,5-*Dimethoxyphenol*.—The epoxide (1.5 g) and 3,5-dimethoxyphenol (1.5 g) were dissolved in benzene (1.5 l) and the mixture divided into five portions. Each portion was irradiated for 0.25 h, the portions combined, and the solvent evaporated. Column chromatography [benzene–acetone (19 : 1)] of the residual solids gave six fractions, R_F 0.45 (70 mg; yellow-brown), 0.39 (210 mg; yellow-brown), 0.27 (75 mg; red-brown), 0.24 (245 mg; brown), 0.21 (320 mg; brown), and 0.16 (210 mg; brown).

The R_F 0.45 fraction afforded 3-(4-methoxyphenyl)-3-(2,4-dimethoxy-6-oxocyclohexa-2,4-dienylidene)-1-(4,6-dimethoxy-2-methoxymethoxyphenyl)propane-1,2-dione (21) as a light yellow *oil*, *m/e* 524 (M^+, 0%), 494 (1.7), 493 (2.3), 374 (1.4), 313 (1.6), 312 (1.7), 300 (15.2), 299 (42), 272 (3.6), 271 (18.0), 226 (56), 225 (100), 195 (65), 193 (55), 181 (37), and 180 (32), δ 7.44, 6.76 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.25, 6.14, 6.01, 5.87 (d, aromatic 3- + 5- + 3′- + 5′-H, *J* 2.5 Hz), 4.91 (s, CH_2), and 3.77, 3.76, 3.63, 3.52, 3.49, 3.36 (s, 6 × OMe), $\nu_{max.}$ 1 710 and 1 813 cm^{-1} (Found: C, 63.8; H, 5.3. $C_{28}H_{28}O_{10}$ requires C, 64.1; H, 5.4%).

The R_F 0.39 fraction gave 2-hydroxy-3-(4-methoxyphenyl)-3-(3,5-dimethoxyphenoxy)-4′,6′-dimethoxy-2′-methoxymethoxypropiophenone (11) as an *oil*, *m/e* 528 (M^+, 100%, field desorption), 374 (31), 273 (16.0), 264 (29), and 225 (15.2); δ 7.21, 6.77 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.30, 6.05 (s, 3′- + 5′-H, *J* 2.5 Hz), 5.85 (m, aromatic 2- + 4- + 6-H), 5.28 (d, 3-H, *J* 2.1 Hz), 5.0 (dd, 2-H, *J* 2.1 and 7.5 Hz), 4.90 (d, CH_2), 6.8 (d, 2-OH, *J* 7.5 Hz), 3.76, 3.71, 3.60 (6 H), and 3.53, 3.30 (s, 6 × OMe); $\nu_{max.}$ 1 718 cm^{-1} (Found: C, 63.3; H, 6.0. $C_{28}H_{32}O_{10}$ requires C, 63.6; H, 6.1%).

Acetylation of propiophenone (11) gave the monoacetate (12) as an amorphous solid, *m/e* 570 (M^+, 100%, field desorption), 416 (48), and 360 (58); δ 7.21, 6.75 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.34, 6.01 (d, aromatic 3′- + 5′-H, *J* 2.5 Hz), 6.17 (d, 2-H, *J* 3.0 Hz), 5.89 (s, aromatic 2- + 4- + 6-H), 5.58 (d, 3-H, *J* 3.0 Hz), 4.98 (s, CH_2), 3.75, 3.71, 3.61 (6 H), 3.58, 3.36 (s, 6 × OMe), and 2.03 (s, 2-OAc).

The R_F 0.27 fraction consisted of 1-(4,6-dimethoxy-2-methoxymethoxyphenyl)-3-(4-methoxyphenyl)-3-(2-hydroxy-4,6-dimethoxyphenyl)propane-1,2-dione (18) as a light yellow *oil*, *m/e* 526 (M^+, 1.1%), 481 (1.2), 301 (2.9), 273 (40), 226 (16.8), 225 (100), 195 (14.9), 181 (19.2), 151 (9.4), and 121 (27); δ 7.01, 6.76 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.31, 6.09, 6.0, 5.97 (d, aromatic 3- + 5-H, 3- + 5-H, *J* 2.5 Hz), 5.0 (s, CH_2), 4.47 (s, enolic OH), 3.76, 3.75, 3.70, 3.67, 3.55, 3.36 (s, 6 × OMe); $\nu_{max.}$ 1 720 cm^{-1} (Found: C, 63.6; H, 5.6. $C_{28}H_{30}O_{10}$ requires C, 63.9; H, 5.7%).

The R_F 0.24 fraction afforded 1-hydroxy-1-(4,6-dimethoxy-2-methoxymethoxyphenyl)-3-(4-methoxyphenyl)-3-(2-hydroxy-4,6-dimethoxyphenyl)propan-2-one (15) as an oil, *m/e* 528 (M^+, 0%), 510 (2.8), 273 (74), 255 (7.3), 227 (100), 225 (89), and 121 (84); δ 8.81 (s, aromatic OH), 7.0, 6.74 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.24, 6.06, 5.94, 5.77 (d, aromatic 3- + 5-H, 3- + 5-H, *J* 2.5 Hz), 5.87 (d, 1-H, *J* 6.9 Hz, collapsed to s in presence of D_2O), 5.71 (s, 3-H), 4.90 (s, CH_2), and 3.75, 3.72, 3.70, 3.44, 3.37, 3.31 (s, 6 × OMe); $\nu_{max.}$ 1 710 cm^{-1}.

Acetylation of propanone (15) gave a solid colourless amorphous diacetate (16), *m/e* 612 (M^+, 0%), 552 (8.3), 315 (89), 273 (87), 269 (100), 227 (97), 225 (43), 209 (46), and 121 (93); δ 7.0, 6.67 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.86 (s, 1-H), 6.25 (s, aromatic 3- + 5-H), 6.22, 6.01 (d, aromatic 3- + 5-H, *J* 2.5 Hz), 5.45 (s, 3-H), 5.0 (s, CH_2), 3.75, 3.72, 3.69 (6 H), 3.62, 3.26 (s, 6 × OMe), 2.17 (s, aromatic OAc), and 1.87 (s, 1-OAc).

The R_F 0.21 fraction was purified by means of p.l.c. [hexane–chloroform–methanol (12 : 7 : 1)] to afford the 2-hydroxy-3-(4-methoxyphenyl)-3-(2-hydroxy-4,6-dimethoxyphenyl)-4′,6′-dimethoxy-2′-methoxymethoxypropiophenone (7) as a light yellow oil, *m/e* 528 (M^+, 0%), 482 (2.1), 274 (26), 273 (76), 272 (5.4), 271 (17), 257 (11), 255 (10), 228 (35), 227 (88), 225 (100), 195 (74), 183 (50), 181 (76), 180 (24), 167 (85), 154 (26), and 121 (80); δ 7.16, 6.75 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.26, 6.02, 5.99, 5.67 (d, aromatic 3- + 5-H, 3- + 5-H, *J* 2.5 Hz), 5.69 (d, 2-H, *J* 3.4 Hz), 5.30 (d, 3-H, *J* 3.4 Hz), 4.91 (s, CH_2), and 3.76, 3.71, 3.66, 3.59, 3.27, 3.19 (s, 6 × OMe); $\nu_{max.}$ 1 682 cm^{-1}.

Methylation of the propiophenone (7) with diazomethane followed by acetylation afforded the monoacetate (8) identical to that previously described.[6]

Acetylation of the R_F 0.21 fraction (38 mg) followed by p.l.c. separation [benzene–acetone (9 : 1)] afforded 2-acetoxy-3-(4-methoxyphenyl)-3-(4-acetoxy-2,6-dimethoxyphenyl)-4′,6′-dimethoxy-2′-methoxymethoxypropiophenone (10) as an amorphous *solid*, R_F 0.50, *m/e* 612 (M^+, 0%), 552 (7.4), 521 (18), 518 (37), 493 (68), 465 (43), 315 (59), 297 (7.1), 273 (61), 225 (100), 209 (13.1), 196 (21), 195 (55), 185 (45), 167 (27), and 121 (64); δ 7.11, 6.64 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.85 (d, 2-H, *J* 8.75 Hz), 6.19, 5.90 (d, aromatic 3- + 5-H, *J* 2.5 Hz), 6.09 (s, aromatic 3- + 5-H), 4.90 (s, CH_2), 4.84 (d, 3-H, *J* 8.75 Hz), 3.72, 3.67, 3.65, 3.55, 3.49, 3.24 (s, 6 × OMe), 2.12 (s, aromatic OAc), and 1.92 (s, 2-OAc) (Found: *m/e* 552.200. $C_{32}H_{36}O_{12}$ requires *M*, 552.199).

The R_F 0.16 fraction afforded 2-hydroxy-3-(4-methoxyphenyl)-3-(4,6-dimethoxy-2-methoxymethoxybenzoyloxy)-4′,6′-dimethoxy-2′-methoxymethoxypropiophenone (13) as an amorphous solid, *m/e* 616 (M^+, 100%, field desorption), 588 (25), 480 (30), 374 (90), 242 (75), and 225 (35); δ([$^2H_6$]-acetone) 7.34, 6.80 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.40—6.13 m, aromatic 3- + 5-H, 3- + 5-H), 6.08 (d, 2-H, *J* 4.8 Hz), 5.10 (s, 2 × CH_2), 5.02 (dd, 3-H, *J* 4.8 and 7.5 Hz), 4.05 (d, 3-OH, *J* 7.5 Hz), 3.79 (6 H), 3.72 (6 H), and 3.69, 3.37, 3.35 (s, 7 × OMe); $\nu_{max.}$ (KBr) 1 717 and 1 735 cm^{-1}

Acetylation of propiophenone (13) gave the monoacetate (13) as an amorphous solid, *m/e* 658 (M^+, 100%, field desorption), 416 (14), 415 (27), 242 (64), and 225 (32); δ 7.27, 6.80 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.40 (d, 3-H, *J* 5.05 Hz), 6.22, 6.20, 6.05, 5.93 (d, aromatic 3- + 5-H, 3- + 5-H, *J* 2.5 Hz), 6.11 (d, 2-H, *J* 5.05 Hz), 5.00 (m, 2 × CH_2), 3.75 (9 H), 3.69, 3.63, 3.37, 3.35 (s, 7 × OMe), and 1.97 (s, 3-OAc).

Acid-catalysed Conversions of the Products of Photolysis

Synthesis of 3-*Hydroxy*-4-(4-*methoxyphenyl*)-5,7-*dimethoxy*-3,4-cis-*dihydrocoumarin* (23).—Propiophenone (7) (20 mg) and toluene-*p*-sulphonic acid (2 mg) in anhydrous benzene (10 ml) were refluxed under nitrogen for 2 h. The mixture was taken up in ether (100 ml), successively washed with 5% sodium hydrogencarbonate (3 × 50 ml) and water (3 × 50 ml), and the solvent evaporated. P.l.c. separation [benzene–acetone (9 : 1) afforded the dihydrocoumarin (23) (R_F 0.34; 8 mg) as an amorphous *solid*, *m/e* 330 (M^+, 8%), 273 (64), 272 (2.8), 271 (8.8), 154 (15.1), and 121 (100); δ 7.37, 6.93 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.35, 6.30 (d, 6- + 8-H, *J* 2.5 Hz), 4.77 (s, 3- + 4-

H), and 3.80, 3.70 (6 H) (s, 3 × OMe); $\nu_{max.}$ 1 775 cm^{-1} (Found: *m/e* 330.111. $C_{18}H_{18}O_6$ requires *M*, 330.109).

Acetylation of the dihydrocoumarin (23) (5 mg) and crystallization from acetone gave the monoacetate as fine *needles*, m.p. 159—161°, *m/e* 372 (M^+, 83%), 312 (98), 284 (98), 273 (19), 271 (60), and 121 (100); δ 7.03, 6.77 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.33, 6.25 (d, 6- + 8-H, *J* 2.5 Hz), 5.75 (d, 3-H, *J* 7.0 Hz), 4.63 (d, 4-H, *J* 7.0 Hz), 3.80, 3.74, 3.70 (s, 3 × OMe), and 2.15 (s, 3-OAc) (Found: C, 64.6; H, 5.4. $C_{20}H_{20}O_7$ requires C, 64.5; H, 5.4%).

The dihydrocoumarin (23; 100 mg) and toluene-*p*-sulphonyl chloride (65 mg) in anhydrous pyridine were stirred at room temperature for 2 h. The product was precipitated with cold 3M-HCl and washed with water. P.l.c. separation [benzene–acetone (9 : 1)] gave the 3-tosyloxy-derivative (25); (80 mg) as a light pink amorphous solid, δ 7.86, 7.33, 7.03, 6.73 (d, 2 aromatic AA′BB′ systems, *J* 8.5 Hz), 6.30 (s, 6- + 8-H), 5.47 (d, 3-H, *J* 6.8 Hz), 4.75 (d, 4-H, *J* 6.8 Hz), 3.77, 3.70 (6 H) (s, 3 × OMe), and 2.40 (s, CH_3).

Synthesis of 2′-Hydroxy-4′,5,6′,7-tetramethoxy-4-(4-methoxyphenyl)flavan-3-one (17).—The propan-2-one (15) (20 mg) and toluene-*p*-sulphonic acid (2 mg) in anhydrous benzene (10 mg) were refluxed under nitrogen for 2 h. The mixture was taken up in ether (100 ml) and successively washed with 5% sodium hydrogencarbonate (3 × 25 ml) and water (3 × 25 ml). Evaporation of the solvent followed by p.l.c. [benzene–acetone (9 : 1)] gave the flavan-3-one (17) (R_F 0.47; 11 mg) as an amorphous *solid*, *m/e* 466 (M^+, 11.0%), 438 (28), 313 (8.7), 312 (24), 285 (10), 284 (10.1), 273 (100), 219 (7.7), 194 (52), 193 (5.7), 180 (10.8), 167 (26), 165 (17), 154 (54), and 121 (91); δ 7.38, 6.83 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.10, 6.02, 6.04, 5.97 (d, aromatic 3- + 5-H, 6- + 8-H, *J* 2.5 Hz), 5.56 (s, 1-H), 4.73 (s, 3-H), and 3.89, 3.76, 3.71, 3.69, 3.68 (s, 5 × OMe); $\nu_{max.}$ 1 718 cm^{-1} (Found: *m/e*, 466.161. $C_{26}H_{26}O_8$ requires *M*, 466.163).

Synthesis of 2-Acetoxy-2-[α-(2-acetoxy-4,6-dimethoxyphenyl)-4-methoxybenzyl]-4,6-dimethoxybenzo[b]furan-3(2H)-one (20).—The α-diketone (18) (25 mg), methanol (2 ml), and 3M-HCl (10 ml) were stirred at ambient temperature for 20 min. The mixture was taken up in ether (100 ml), washed with water (3 × 50 ml), and the solvent evaporated. P.l.c. separation [benzene–acetone (8 : 2)] gave an impure sample of the benzofuranone (19) (R_F 0.31; 15 mg). Acetylation of this fraction followed by p.l.c. separation [benzene–acetone (9 : 1)] afforded the diacetate (20) (R_F 0.39, 15 mg) as an amorphous *solid*, *m/e* 566 (M^+, 0%), 506 (9.9), 464 (9.0), 447 (26), 316 (40), 315 (100), 284 (15.7), 274 (31), 273 (92), 271 (13.3), 257 (6.3), 209 (5.3), 181 (21), 149 (34), and 121 (78); δ 7.37, 6.73 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.13, 5.85 (d, 5- + 7-H, *J* 2.5 Hz), 6.01, 5.99 (d, aromatic 3- + 5-H, *J* 2.5 Hz), 5.20 (s, α-H), 3.79, 3.76, 3.74, 3.65 (6 H) (s, 5 × OMe), 2.09 (s, aromatic OAc), and 2.04 (s, 2-OAc) (Found: C, 63.4; H, 5.4. $C_{30}H_{30}O_{11}$ requires C, 63.6; H, 5.3%).

Synthesis of 4′,5,7-Trimethoxyisoflavone (27) *and* (±)-3-*Hydroxy-4′,5,7-trimethoxy-2,3-trans-flavanone* (28).—The 3-benzoyloxypropiophenone (13) (120 mg) was stirred in ethanol (15 ml) and 3M-HCl (0.1 ml) at room temperature for 2 h. The mixture was taken up in ether (100 ml), washed with water (5 × 50 ml), and the solvent evaporated. P.l.c. separation [benzene–acetone (19 : 1)] followed by crystallization from acetone gave the triol (46) (R_F 0.24; 42 mg) as *needles*, m.p. 210—203°, *m/e* 528 (M^+, 0%, appearance potential), 392 (29), 330 (38), 209 (13), 198 (60), 194 (26), 181 (100), 148 (15), 136 (25), 122 (33), and 121 (21); δ 11.01, 9.31 (s, 2 × OH), 7.41, 6.85 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.19 (d, 2-H, *J* 1.9 Hz), 6.07, 5.97, 5.90, 5.89 (d, aromatic 3- + 5-H, 3- + 5-H, *J* 2.5 Hz), 5.47 (dd, 3-H, *J* 10.0 and 1.9 Hz), 4.07 (d, OH, *J* 10.0 Hz), and 3.87, 3.81, 3.79, 3.77, 3.75 (s, 5 × OMe); $\nu_{max.}$ 1 625 cm^{-1} (Found: C, 61.3; H, 5.3. $C_{27}H_{28}O_{11}$ requires C, 61.4; H, 5.3%).

The 3-benzoyloxypropiophenone (46) (20 mg) and toluene-*p*-sulphonic acid (1 mg) in anhydrous benzene (25 ml) were refluxed for 1 min and the mixture taken up in ether (50 ml). The extract was successively washed with 5% sodium hydrogencarbonate (3 × 10 ml) and water (3 × 50 ml) and the solvent evaporated. P.l.c. separation [benzene–acetone (9 : 1)] afforded three fractions, R_F 0.55 (6 mg; red-brown), 0.63 (4 mg; red-brown), and 0.15 (2 mg; brown).

Crystallization of the former from methanol gave the isoflavone (27) as light yellow needles, m.p. 160—161° (lit.,[18] 162—163°), while the R_F 0.63 fraction afforded the flavanone (28) as white needles (from methanol), m.p. 140—141° (lit.,[19] 141—143°). 2-Hydroxy-4,6-dimethoxybenzoic acid crystallized from the R_F 0.15 band [ether-benzene (1 : 1)], m.p. 153—155° (lit.,[20] 152—154°).

The chalcone epoxide (1) (200 mg) and 2,4,6-trihydroxybenzoic acid (200 mg) in acetone (50 ml) were stirred at room temperature for 1 h. The mixture was diluted with water (100 ml) and extracted with ether (3 × 50 ml). The ethereal layer was washed with 5% sodium hydrogencarbonate (3 × 25 ml), water (3 × 50 ml), and the solvent evaporated. P.l.c. separation [benzene–acetone (9 : 1)] of the residual solids followed by crystallization of the R_F 0.42 fraction (142 mg) from acetone, afforded the 3-benzoyloxypropiophenone (45) as needles, m.p. 168—172°, δ 9.56 (s, 3 × OH), 7.38, 6.81 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.20 (d, 2-H, *J* 1.25 Hz), 6.01, 5.89m(d, aromatic 3- + 5-H), 5.79 (s, aromatic 3- + 5-H), 5.42 (d, 3-H, *J* 1.25 Hz), and 3.76, 3.75, 3.71 (s, 3 × OMe).

Methylation of the β-ester (45) with diazomethane in dry ethereal solution gave a dimethyl ether identical with the trihydroxy-β-ester (46).

Acid treatment of the 3-benzoyloxypropiophenone (45) (50 mg) and work-up as described for the analogous (46), affords the isoflavone (27) in 48% yield.

The chalcone epoxide (1) (500 mg) and 2,4,6-trihydroxybenzoic acid (270 mg) in acetone (25 ml) stirred at room temperature for 20 min gives the 2′-methoxymethoxy analogue (47) [308 mg; R_F 0.53 in benzene–acetone (4 : 1 v/v]. Its fully methylated ether (48) in $CDCl_3$–C_6D_6 (3 : 2 v/v) with added D_2O, exhibits a broadened downfield doublet (δ 6.10, *J* 3.5 Hz) as well as its sharp counterpart (δ 5.05, *J* 3.5 Hz) in an AB system, which after acetylation undergoes shifts in $CDCl_3$ to δ 6.40 (broadened) and 6.08 (sharp), respectively (*J* 6.7 Hz). These resonances, assigned to 3- and 2-H, respectively, on the basis of benzylic coupling of the former, provide proof of the β-ester assignment of (47) and (48) [and hence of (45), (46), and (13)] as anticipated from the above reactions.

Acid-catalysed Coupling of Phloroglucinol to Ethyl 3-(4-*Methoxyphenyl*)-2,3-*epoxypropionate* (29)

Synthesis of the 4-*Aryl*-3-*hydroxydihydrocoumarin Pair* (23) *and* (33).—The epoxycinnamate[12] (29) (500 mg) and phloroglucinol (1 g) in anhydrous diethyl ether (50 ml) and acetic acid (0.1 ml) were stirred at room temperature for 96 h. The mixture was taken up in ethyl acetate (50 ml), washed with water (5 × 20 ml), and the solvent evaporated. P.l.c. separation [chloroform–acetone (8 : 2)] afforded three bands, R_F 0.43 (56 mg; red-brown), 0.37 (59 mg; red), and 0.31 (50 mg; red).

The R_F 0.31 fraction gave (±)-ethyl 2-hydroxy-3-(4-methoxyphenyl)-3-(2,4,6-trihydroxyphenyl)propionate (32) as a light pink amorphous *solid*, *m/e* 348 (M^+, 0%), 330 (3.1), 303 (22), 302 (79), 247 (12), 246 (73), 245 (100), 243 (29), 229 (11), 213 (30), 165 (36), and 121 (13); δ([$^2H_6$]-acetone) 8.69 (s, 2 × OH), 7.97 (s, OH), 7.40, 6.80 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 5.97 (s, aromatic 3- + 5-H), 5.33 (d, 2-H, *J* 4.8 Hz), 5.17 (d, 3-H, *J* 4.8 Hz), 4.05 (q, CH_2, *J* 7.0 Hz), 3.75 (s, OMe), and 1.08 (t, CH_3, *J* 7.0 Hz); $\nu_{max.}$ (KBr) 1 735 cm^{-1} (Found: C, 62.2; H, 5.9. $C_{18}H_{20}O_7$ requires C, 62.1; H, 5.8%).

The 2-hydroxypropionate (32) (10 mg) and 0.05M-H_2SO_4 were stirred in dry ether (5 ml) for 2 h at room temperature. Work-up as above followed by methylation with methyl iodide and p.l.c. separation [benzene–acetone (9 : 1)] gave the 3,4-*cis*-dihydrocoumarin (23) (7 mg).

The R_F 0.37 fraction afforded the 2-hydroxy-3,3-diaryl-propionate (31) as a light pink amorphous *solid*, *m/e* 348 (M^+, 0%), 303 (15), 302 (70), 246 (47), 245 (100), 243 (18), 213 (20), 165 (24), and 121 (13); δ([$^2H_6$]acetone) 7.93 (s, 3 × OH), 7.31, 6.71 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 5.93 (s, aromatic 3- + 5-H), 5.22 (d, 2-H, *J* 5.8 Hz), 4.95 (d, 3-H, *J* 5.8 Hz), 4.13 (q, CH_2, *J* 7.0 Hz), 3.73 (s, OMe), 1.13 (t, CH_3, *J* 7.0 Hz); $\nu_{max.}$ (KBr) 1 735 cm^{-1} (Found: C, 62.1; H, 5.8. $C_{18}H_{20}O_7$ requires C, 62.1; H, 5.8%).

Similar treatment of (31) as was described for propionate (32) gave the 3,4-*trans*-dihydrocoumarin (33).

The R_F 0.43 fraction gave the 3-(3,5-dimethoxyphenoxy)-propionate (30) as a light pink amorphous *solid*, *m/e* 348 (M^+, 0%), 302 (7), 246 (13), 245 (34), 243 (10), 224 (16), 223 (89), 222 (35), 161 (28), 135 (22), 126 (31), and 121 (100); δ([$^2H_6$]acetone) 8.10 (s, 2 × OH), 7.40, 6.90 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 5.95 (s, aromatic 2- + 4- + 6-H), 5.43 (d, 2-H, *J* 4.3 Hz), 4.37 (m, 3-H, 2-OH), 4.10 (q, CH_2, *J* 7.0 Hz), 3.77 (s, OMe), 1.12 (t, CH_3, *J* 7.0 Hz); $\nu_{max.}$ (KBr) 1 750 cm^{-1} (Found: C, 62.0; H, 5.7. $C_{18}H_{20}O_7$ requires C, 62.1; H, 5.8%).

Acid treatment of the 3-aryloxypropionate (30) followed by methylation as above also gave the 3,4-*cis*-coumarin (23).

Condensation of phloroglucinol (1 g) and the epoxy-cinnamate (29) (1 g) in anhydrous diethyl ether (50 ml) and H_2SO_4 [0.1 ml in ether (10 ml)] for 96 h at room temperature and worked-up as above followed by p.l.c. separation [chloroform–acetone (8 : 2)] gave two fractions, R_F 0.25 (310 mg, brown) and 0.17 (280 mg, brown).

Crystallization of the latter from chloroform–acetone (7 : 3) gave the 3,4-*trans*-4-(4-methoxyphenyl)-3,5,7-tri-hydroxydihydrocoumarin as *needles*, m.p. 201—203°, *m/e* 302 (M^+, 75%), 246 (54), 245 (100), 213 (19), 165 (26), 138 (22), 126 (85), and 121 (35); δ([$^2H_6$]acetone) 8.55 (s, 2 × OH), 7.07, 6.82 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.32, 6.18 (d, 6- + 8-H, *J* 2.5 Hz), 5.44 (s, 3-OH), 4.52 (d, 4-H, *J* 2.7 Hz), 4.43 (d, 3-H, *J* 2.7 Hz), 3.77 (s, OMe); $\nu_{max.}$ (KBr) 1 773 cm^{-1} (Found: C, 63.4; H, 4.7. $C_{16}H_{14}O_6$ requires C, 63.6; H, 4.7%).

Methylation of the phenolic 3,4-*trans*-dihydrocoumarin with methyl iodide followed by crystallization from acetone afforded 3,4-*trans*-3-hydroxy-4-(4-methoxyphenyl)-5,7-di-methoxydihydrocoumarin (33) as needles, m.p. 162—163°, *m/e* 330 (M^+, 38%), 274 (19), 273 (100), 193 (11), and 121 (70); δ 7.03, 6.78 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.37, 6.28 (d, 6- + 8-H, *J* 2.5 Hz), 4.50 (s, 3- + 4-H), and 3.82, 3.75, 3.68 (s, 3 × OMe); $\nu_{max.}$ 1 775 cm^{-1} (Found: *m/e*, 330.109. $C_{18}H_{18}O_6$ requires *M*, 330.109).

Acetylation of the trimethoxydihydrocoumarin (33) and crystallization from methanol gave the monoacetate (34) as *needles*, m.p. 154—156°, *m/e* 372 (M^+, 30%), 326 (18), 312 (100), 284 (96), 273 (43), 272 (17), 271 (43), and 121 (84); δ 7.01, 6.77 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.37, 6.28 (d, 6- + 8-H, *J* 2.5 Hz), 5.53 (d, 3-H, *J* 2.7 Hz), 4.57 (d, 4-H, *J* 2.7 Hz), 3.83, 3.75, 3.68 (s, 3 × OMe), and 2.03 (s, 3-OAc) (Found: C, 64.5; H, 5.4. $C_{20}H_{20}O_7$ requires C, 64.5; H, 5.4%).

Treatment of the 3,4-*trans*-dihydrocoumarin (33) with toluene-*p*-sulphonyl chloride as was described for the 3,4-*cis*-analogue (23) gave the 3-tosyloxy-derivative (35) as a light pink amorphous solid, δ 7.70, 7.25, 6.87, 6.70 (d, 2 aromatic AA′BB′ systems, *J* 8.5 Hz), 6.20 (s, 6- + 8-H), 5.03 (d, 3-H, *J* 2.7 Hz), 4.66 (d, 4-H, *J* 2.7 Hz), 3.77, 3.69, 3.65 (s, 3 × OMe), and 2.41 (s, Me).

The R_F 0.17 fraction afforded the free phenolic 3,4-cis-*dihydrocoumarin*, m.p. 196—198° (from acetone), *m/e* 302 (M^+, 82%), 246 (74), 245 (100), 213 (26), 165 (42), 138 (20), 123 (13), and 121 (17); δ([$^2H_6$]acetone) 8.68 (s, 2 × OH), 7.08, 6.77 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.31, 6.21 (d, 6- + 8-H, *J* 2.5 Hz), 4.87 (d, 3-H, *J* 6.8 Hz), 4.62 (d, 4-H, *J* 6.8 Hz), 4.34 (s, 3-OH), and 3.68 (s, OMe); $\nu_{max.}$ (KBr) 1 773 cm^{-1} (Found: C, 63.5; H, 4.6. $C_{16}H_{14}O_6$ requires C, 63.6; H, 4.7%).

Methylation of the R_F 0.17 fraction with methyl iodide gave the 2,3-*cis*-dihydrocoumarin (23).

Synthesis of the 3-*Aryl*- (36) *and* 3-*Hydroxy-coumarins* (26).—The 3,4-*trans*-dihydrocoumarin (33) (100 mg) in anhydrous benzene (50 ml) and H_2SO_4 (0.2 ml diluted to 5 ml in benzene) was refluxed for 3 h. The mixture was taken up in ethyl acetate (50 ml), washed with water (3 × 50 ml), and the solvent evaporated. P.l.c. separation [benzene–acetone (19 : 1)] followed by crystallization from acetone, gave 3-(4-methoxyphenyl)-5,7-dimethoxycoumarin (36) (R_F 0.38; 26 mg) as needles, m.p. 164—166° (lit.,[21] 166—168°), *m/e* 312 (M^+, 100%), 298 (35), 297 (63), 284 (44), 270 (37), 269 (63), 241 (29), 226 (43), and 142 (44); δ 8.05 (s, 4-H), 7.66, 6.95 (d, aromatic 2- + 6-H, 3- + 5-H, *J* 8.5 Hz), 6.45, 6.36 (d, 6- + 8-H, *J* 2.5 Hz), and 3.91, 3.86, 3.84 (s, 3 × OMe) (Found: C, 69.2; H, 5.2. $C_{18}H_{16}O_5$ requires C, 69.2; H, 5.2%).

Irradiation of the 3,4-*trans*-3-tosyloxydihydrocoumarin (35) for 20 min at 300 nm followed by evaporation of the solvent and p.l.c. separation [benzene–acetone (19 : 1)] also gave the 3-arylcoumarin (36) (35 mg).

Acid treatment of the 3,4-*cis*-dihydrocoumarin (23) (100 mg) and work-up as was described for the 3,4-*trans*-analogue (33) followed by crystallization from methanol, gave 3-hydroxy-5,7-dimethoxycoumarin (26) (R_F 0.22, 35 mg) as *needles*, m.p. 188—189°, *m/e* 222 (M^+, 100%), 207 (24), and 179 (28); δ([$^2H_6$]DMSO) 7.06 (s, 4-H), 6.52, 6.46 (d, 6- + 8-H, *J* 2.5 Hz), and 3.91, 3.79 (s, 2 × OMe) (Found: C, 59.4; H, 4.5. $C_{11}H_{10}O_5$ requires C, 59.5; H, 4.5%).

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