Photochemical Equivalent of a Benzilic Acid Rearrangement and Related Conversions

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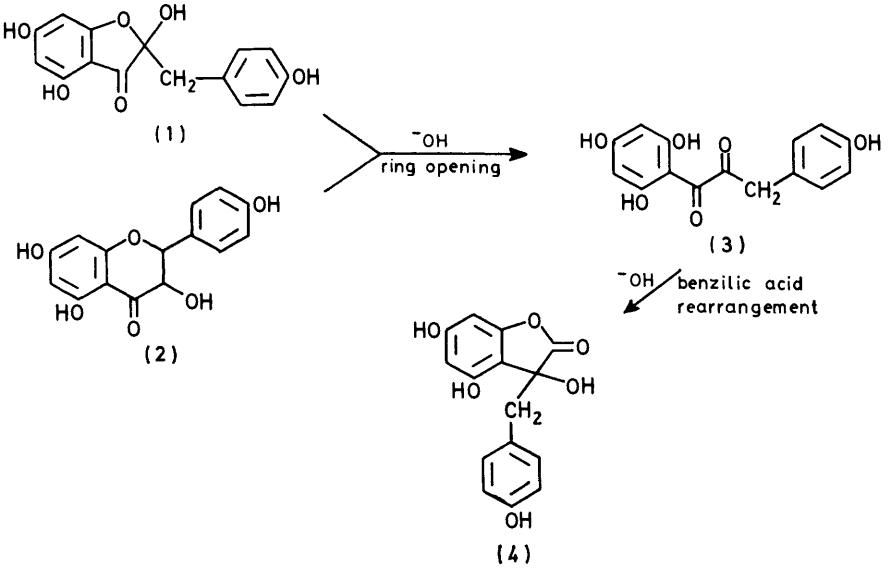
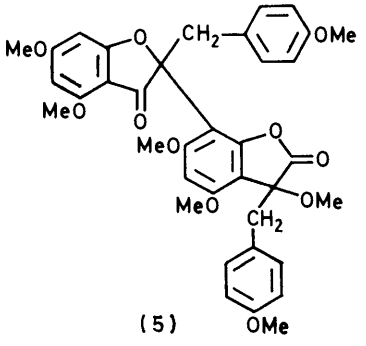
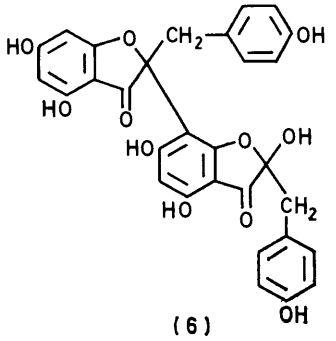
Irradiation of a 2-benzyl-2-hydroxybenzo[*b*]furan-3(2*H*)-one in acetone–water results in the equivalent of a benzilic acid rearrangement of the aryl benzyl α-diketone formed from homolysis of the heterocycle, to give the 3-benzyl-3-hydroxybenzo[*b*]furan-2(3*H*)-one analogue.

THE benzilic acid rearrangement of 2-benzyl-2-hydroxybenzo[*b*]furan-3(2*H*)-ones [*e.g.* maesopsin (1)] and 3-hydroxyflavanones [*e.g.* (2)] to 3-benzyl-3-hydroxybenzo[*b*]furan-2(3*H*)-ones (4), presumably *via* an α-diketone intermediate (3), is an established reaction common to both flavonoids.[1-4] This knowledge led to to the surmise that the biflavonoid derivative (5) [a combination of units (1) and (4)], recently obtained after methylation of a fraction of the extractives from *Berchemia zeyheri* rich in zeyherin (6), is an artefact.[5] However, consideration of the anhydrous conditions (dimethyl sulphate, dry acetone, and anhydrous potassium carbonate) used during the methylation, and hence of the need to establish the full range of conditions which could result in the presumed rearrangement, led us to carry out the conversions shown in the Scheme.



Irradiation of 2,4,4′,6-tetra-*O*-methylmaesopsin (7) in acetone–water, tetrahydrofuran–water, or dioxan–water at 350 nm gives 4,4′,6-tri-*O*-methylmaesopsin (8), a novel reaction equivalent to 2-ether fission. 2′-Hydroxy-α,4,4′,6′-tetramethoxy-*cis*-chalcone (16) is also formed





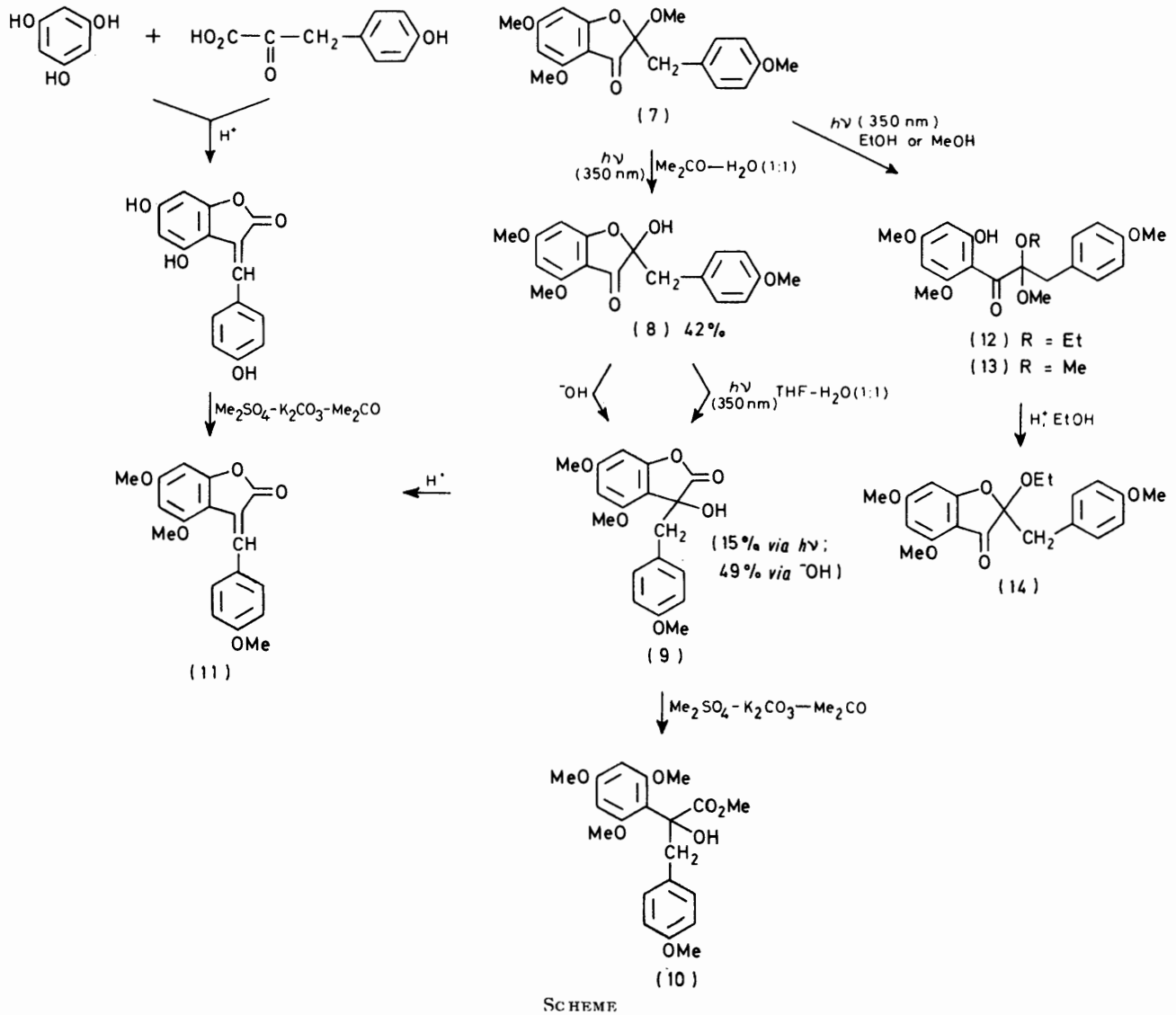
[1] G. B. Guise, E. Ritchie, and W. C. Taylor, *Austral. J. Chem.*, 1962, **15**, 314.

[2] N. F. Janes, F. E. King, and J. W. W. Morgan, *J. Chem. Soc.*, 1963, 1356.

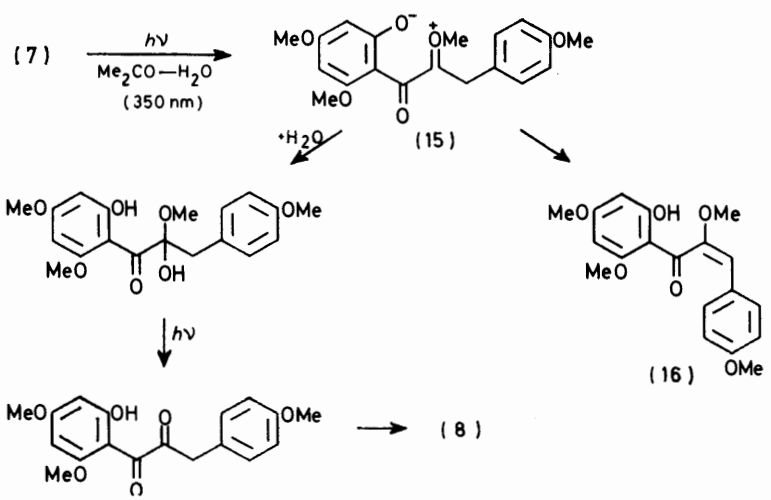
[3] T. Oyamada, *Annalen*, 1939, **538**, 44.

[4] D. Molho, J. Coillard, and C. Mentzer, *Bull. Soc. chim. France*, 1954, 1397.

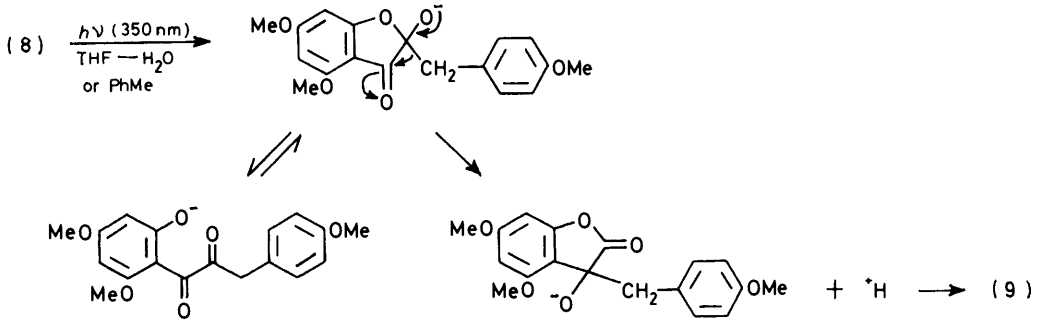
[5] F. du R. Volsteedt, Ph.D. Thesis, University of the Orange Free State, Bloemfontein, February, 1976.



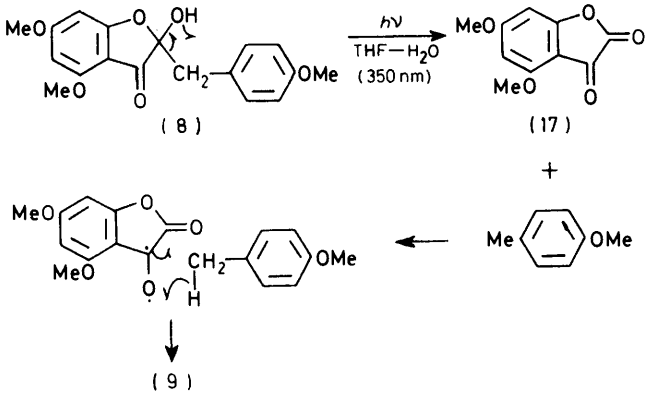
SCHEME



in minor proportion in a competing reaction, but is significantly the sole product in the absence of water. The primary step in the suggested mechanism (7) ⟶ (15) ⟶ (8) or (16) represents fission of a heterocyclic C–O bond attached to an α-carbon atom (*cf.* ref. 6). Its occurrence is substantiated by using methanol as trapping agent, when a 3-aryl-2,2-dimethoxypropiophenone (13) results, as shown previously.[7] Both reactions may now be rationalized by invoking (*cf.* ref. 8) a zwitterionic intermediate state (15) of the diradical formed on C–O bond homolysis.

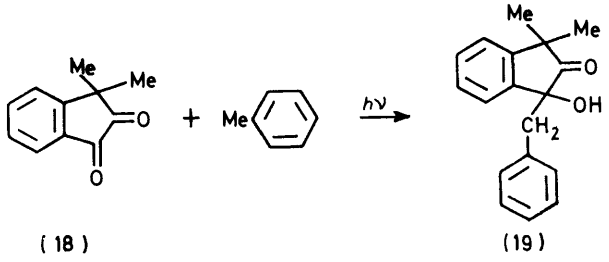


Irradiation of the product (8) under identical conditions, but in dry toluene or in tetrahydrofuran–water, gives a photochemical rearrangement in low yield (15%) to the 3-benzyl-3-hydroxybenzo[*b*]furan-2(3*H*)-one analogue (9). The conversion presumably proceeds *via* a 1,2-shift in the sequence (8) ⟶ (9), following photochemical dissociation (*cf.* ref. 9). Alternatively the reaction may proceed through a benzofuran-2,3-dione (17) and *O*-methyl-*p*-cresol, a mechanism derived from



the work of Rigaudy and Paillous,[10] who established that irradiation of 3,3-dimethylindane-1,2-dione (18) in toluene in the near-u.v. region gives 1-benzyl-1-hydroxy-3,3-dimethylindan-2-one (19) in 51% yield. However, simple β-fission of the 2-benzyl-2-hydroxybenzofuran-3-one (8), as illustrated in the latter mechanism, appears unlikely. Its photolysis to the isomeric 3-benzyl-3-hydroxybenzofuran-2-one (9) accordingly represents the first reported photochemical equivalent of an acknowledged benzilic acid rearrangement, and also a novel example of photolytic cleavage of bonds attaching α-substituents (*cf.* ref. 6). The conventional rearrangement with alkali when applied to the identical compound (8) gives a much higher (49%) yield of the benzofuran-2-one (9).

Confirmation of structure was also obtained by treatment of the lactone (9) with mineral acid: elimination of water gives the 3-benzylidenebenzofuran-2-one analogue (11) which could be synthesised in 52% yield by direct acid-catalysed condensation of *p*-hydroxyphenylpyruvic acid with phloroglucinol under aqueous conditions, followed by methylation of the free phenol with dimethyl sulphate (*cf.* Scheme). This ready reaction is



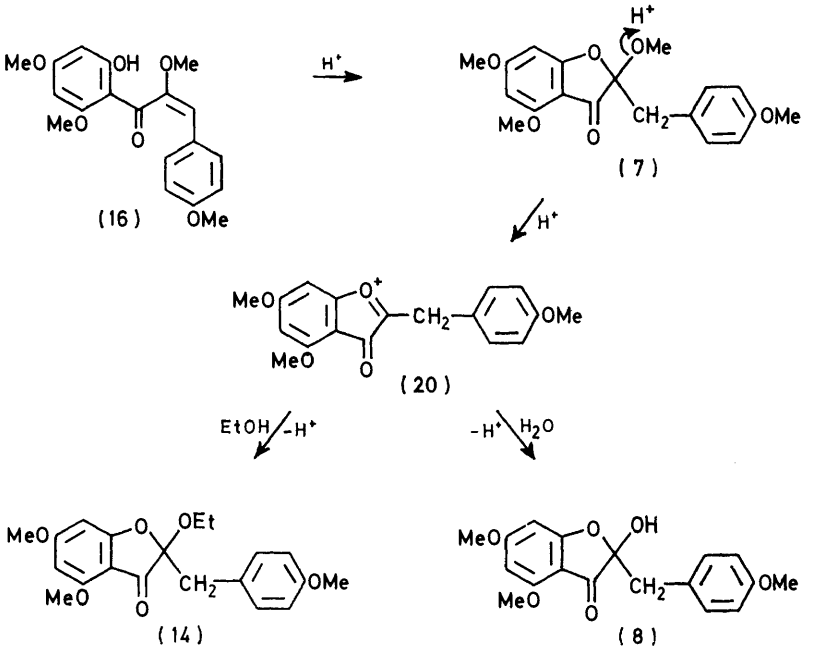
analogous to an earlier condensation by Molho *et al.*[6] of resorcinol with phenylpyruvic acid in dichloromethane using a Lewis acid ($AlCl_3$). The condensation holds some biogenetic interest in view of the purported role of *p*-hydroxyphenylpyruvic acid in flavonoid biosynthesis.[11] Methylation of the free phenol with diazomethane in place of dimethyl sulphate in the final step was unsatisfactory, owing to methylene insertion reactions (*cf.* ref. 12) in addition to *O*-methylation.

Treatment of 3-benzyl-3-hydroxybenzofuran-2-one (9) with anhydrous potassium carbonate–dimethyl sulphate in dry acetone (conventional methylation procedure) causes opening of the lactone ring to give the methyl

[6] K. Schaffner and O. Jeger, *Tetrahedron*, 1974, **30**, 1891.
[7] T. G. Fourie, D. Ferreira, and D. G. Roux, *J.C.S. Perkin I*, 1977, 125.
[8] L. Salem, *Israel. J. Chem.*, 1975, **14**, 89; *Science*, 1976, **191**, 822.
[9] C. H. Depuy and O. L. Chapman, ' Molecular Reactions and Photochemistry,' Prentice-Hall, New York, 1972, p. 67.
[10] J. Rigaudy and N. Paillous, *Bull. Soc. chim. France*, 1971, 576, 585.
[11] E. W. Underhill, J. E. Watkin, and A. C. Neish, *Canad. J. Biochem. Physiol.*, 1957, **35**, 219, 229; D. G. Roux and D. Ferreira, *Phytochemistry*, 1974, **13**, 2039.
[12] E. V. Brandt, D. Ferreira, and D. G. Roux, *Chem. Comm.*, 1971, 116.

ester of 2-hydroxy-3-(4-methoxyphenyl)-2-(2,4,6-trimethoxyphenyl)propionic acid (10). The acid represents the methylated derivative of the product of benzilic acid rearrangement of tri-*O*-methylmaesopsin (8) prior to lactonization.

Remarkably, the heterocycle of the related unit of the biflavonoid (5) remained unhydrolysed under identical conditions, and the tertiary hydroxy-function of the ester (10) remains unmethylated in contrast to the existence of a tertiary methoxy-group in the biflavonoid. These differences are unexplained at present, but the former may be related to the effects of extremes of atmospheric humidity, which are difficult to avoid.



Irradiation of tetra-*O*-methylmaesopsin (7) at 350 nm in ethanolic solution results in solvolysis of the heterocycle as previously observed [7] to form the 3-aryl-2-ethoxy-2-methoxypropiophenone (12), presumably as a result of the reaction of ethanol with the zwitterion (15). Introduction of the ethoxy-function thus reaffirms the formation of this intermediate. The corresponding acetal (13) (*cf.* Scheme) formed in methanol [7] permits easy access to 2-*O*-ethyl-4,4′,6-tri-*O*-methylmaesopsin (14) by ethanolysis, presumably *via* an oxonium intermediate [*cf.* (20)].

Alternative routes to tri-*O*-methylmaesopsin (8) and its 2-*O*-ethyl derivative are available under ionic conditions by using the 2′-hydroxy-α-methoxy-*cis*-chalcone as starting material in the sequence (16) ⟶ (7) ⟶ (20) ⟶ (14) and (8), all three products being formed in acidified aqueous ethanol.

Chemical shifts of methine protons in $CDCl_3$ are useful for distinguishing amongst 3-benzylidenebenzofuran-2-ones (τ 2.10), 2-benzylidenebenzofuran-3-ones (aurones) (3.27), flavones (3.50), and isoflavones (2.18) with the same trimethoxybenzenoid substitution pattern.

EXPERIMENTAL

Irradiation of compounds in methanolic solution in a quartz vessel was carried out in a slow current of nitrogen (*ca.* 1 ml min^{-1}) in a Rayonet photochemical reactor. T.l.c. was performed on DC-Plastikfolien Kieselgel 60 F_{254} (0.25 mm); for preparative scale experiments (p.l.c.) Kieselgel PF_{254} was used. Preparative plates were air-dried, used without prior activation, and sprayed with H_2SO_4–HCHO (40 : 1) after development. Colours indicated are those obtained with this reagent. Evaporations were carried out under reduced pressure with a water-bath temperature of 60 °C. Methylations were performed with an excess of diazomethane in methanol–diethyl ether at −15 °C for 48 h, or with dimethyl sulphate in dry acetone–anhydrous potassium carbonate under reflux. Mass spectral data were recorded with a Varian CH-5 spectrometer, and n.m.r. spectra with a Varian T-60 spectrometer. Analyses (C and H) were performed by the National Chemical Research Laboratory, C.S.I.R., Pretoria, and by Alfred Bernhardt, Bonn.

Isolation of Maesopsin {(±)-2-(4′-*Hydroxybenzyl*)-2,4,6-*trihydroxybenzo*[b]*furan*-3(2H)-*one*} (1).—Drillings (2 kg) from the red heartwood of *Berchemia zeyheri* [1,5] were dewaxed by elution with n-hexane (2 × 1.5 l) for two 24 h periods at ambient temperature. After drying in air the drillings were extracted with methanol (3 × 1.5 l) for three 24 h periods at room temperature. Evaporation left a residue which was redissolved in ethyl acetate. Maesopsin was extracted with aqueous 10% sodium hydrogen carbonate [1] (2 ×). Acidification of the aqueous layer, extraction with ethyl acetate, and evaporation of the organic phase gave a red amorphous solid. Crystallization from methanol gave white cubes (5 g), m.p. 218—220° (lit.,[2] 218—220°).

(±)-2,4,4′,6-*Tetra*-O-*methylmaesopsin* (7).—Treatment of maesopsin with dimethyl sulphate gave the fully methylated derivative as pale yellow cubic crystals (5 g), m.p. 130.4° (from methanol) (lit.,[1] 130—131°), shown to be optically inactive by both o.r.d. and c.d. examination in methanol

(JASCO J-20 spectropolarimeter). The structure was confirmed by n.m.r. and mass spectrometry.[13]

Irradiation of 2,4,4′,6-*Tetra*-O-*methylmaesopsin.*—(a) *In solvent–water systems.* Tetra-*O*-methylmaesopsin (500 mg) in acetone–water (1 : 1 v/v; 100 ml) was irradiated at 350 nm for 5.5 h under nitrogen. The acetone was removed under reduced pressure, and the product extracted with ether. P.l.c. in benzene–acetone (9 : 1 v/v) gave three products, R_F 0.67, 0.42, and 0.15.

2′-*Hydroxy*-α,4,4′,6′-*tetramethoxy*-cis-*chalcone* (16).—The fraction (90 mg) R_F 0.67, red-brown with the spray reagent, crystallized from methanol as orange-yellow needles (75 mg, 15%), m.p. 110.5° (lit.,[7] 116°). Spectra were identical with those reported.[7]

(±)-4,4′,6-*Tri*-O-*methylmaesopsin* (8).—The fraction (243 mg) R_F 0.15, dark red with the spray reagent, crystallized from methanol as fine white needles (210 mg, 42%), m.p. 162.8° (lit.,[2] 144—145°; lit.,[1,14] 158—159°) (Found: M^+, 330.108; C, 65.4; H, 5.5%. Calc. for $C_{18}H_{18}O_6$: *M*, 330.100; C, 65.4; H, 5.5%); *m/e* 330 (18.2%), 209 (69), 181 (100), and 121 (90); τ ($CDCl_3$) 2.78 (d, 2′- + 6′-H, *J* 8.0 Hz), 3.23 (d, 3′- + 5′-H, *J* 8.0 Hz), 3.95 and 4.12 (dd, 5- + 7-H, *J* 2.0 Hz), *ca.* 5.85br (s, OH), 6.17 (s, 2 × OMe), 6.25 (s, OMe), and 6.84 (s, CH_2); $\nu_{max.}$ ($CHCl_3$) 1 710 cm^{-1} (C=O in 5-membered heterocycle).

The fraction (128 mg) R_F 0.42, red with the spray reagent, was unchanged tetra-*O*-methylmaesopsin.

The same products were formed when dioxan–water or tetrahydrofuran (THF)–water (1 : 1 v/v) was used.

(b) *In tetrahydrofuran.* Tetra-*O*-methylmaesopsin (100 mg) in THF (100 ml) was irradiated at 350 nm for 4 h under nitrogen. Evaporation left two compounds. P.l.c. (benzene–acetone, 9 : 1 v/v) gave 2′-hydroxy-α,4,4′,6′-tetramethoxy-*cis*-chalcone, R_F 0.67 (60 mg, 60%), and starting material, R_F 0.42 (13 mg).

Acidic Hydrolysis of 2′-*Hydroxy*-α,4,4′,6′-*tetramethoxy*-cis-*chalcone.*—The α-methoxychalcone (400 mg) in ethanol (25 ml) and 3N-sulphuric acid (5 ml) was refluxed for 2 h. The ethanol was evaporated off and the product was extracted with ether; the extract was washed acid-free with water. P.l.c. (benzene–acetone, 85 : 15 v/v) of the recovered solid gave three products, *R*– 0.67, 0.60, and 0.34.

(±)-2-O-*Ethyl*-4,4′,6-*tri*-O-*methylmaesopsin* (14). The fraction R_F 0.67, orange red with the spray reagent, gave white *plates* (40 mg, 10%), m.p. 131° (from methanol) (Found: M^+, 358.143; C, 66.9; H, 6.4%. $C_{20}H_{22}O_6$ requires *M*, 358.142; C, 67.0; H, 6.2%); *m/e* 358 (39%), 313 (9.1), 237 (62), 209 (100), 180 (41), and 121 (58); τ ($CDCl_3$) 2.83 (d, 2′- + 6′-H, *J* 8.5 Hz), 3.28 (d, 3′- + 5′-H, *J* 8.5 Hz), 3.95 and 4.12 (dd, 5- + 7-H, *J* 2.0 Hz), 6.17 (s, 2 × OMe), 6.30 (s, OMe), 6.52 (q, OCH_2, *J* 7.5 Hz), 6.86 (s, CH_2), and 8.86 (t, CH_3, *J* 7.5 Hz); $\nu_{max.}$ ($CHCl_3$) 1 710 cm^{-1} (C=O in 5-membered ring).

(±)-2,4,4′-6-*Tetra*-O-*methylmaesopsin* (7). The fraction R_F 0.60, red with the spray reagent, crystallized from methanol as pale yellow cubes (40 mg, 10%), m.p. 130.4°, identical with the compound described above.

(±)-4,4′,6-*Tri*-O-*methylmaesopsin* (8). The fraction R_F 0.34, dark red with the spray reagent, yielded fine white needles (240 mg, 60%), m.p. 162° (from methanol), identical with the compound described above.

Irradiation of (±)-4,4′,6-*Tri*-O-*methylmaesopsin* (8).—4,4′,6-Tri-*O*-methylmaesopsin (100 mg) in tetrahdyrofuran–water (1 : 1 v/v; 100 ml) was irradiated for 16 h at 350 nm under nitrogen. The solution was evaporated and the recovered solid separated into two products, R_F 0.37 and 0.23, by p.l.c. in benzene–acetone (9 : 1 v/v).

(±)-3-*Hydroxy*-4,6-*dimethoxy*-3-(4-*methoxybenzyl*)*benzo*[b]*furan*-2(3H)-*one* (9). The fraction R_F 0.37, olive-green with the spray reagent, was isolated as an amorphous pale yellow *solid* (15 mg, 15%) (Found: C, 65.2; H, 5.6. $C_{18}H_{18}O_6$ requires C, 65.4; H, 5.5%); *m/e* 312 (9.7%) (M^+ − 18), 209 (64), and 121 (100); τ ($CDCl_3$) 3.17 (d, 2′- + 6′-H, *J* 8.0 Hz), 3.40 (d, 3′- + 5′-H), 3.79 and 3.93 (dd, 5- + 7-H, *J* 2.0 Hz), 6.07, 6.26, and 6.31 (s, 3 × OMe), 6.0—6.8br (s, OH), and 6.40 and 6.75 (dd, CH_2, *J* 14.0 Hz); $\nu_{max.}$ ($CHCl_3$) 1 820 cm^{-1} (C=O of lactone).

The fraction R_F 0.23 (20 mg) was starting material.

Irradiation of 4,4′,6-tri-*O*-methylmaesopsin in dry toluene for 11 h gave the same yield of rearrangement product.

Alkaline Hydrolysis of 4,4′,6-*Tri*-O-*methylmaesopsin* (*Benzilic Acid Rearrangement*).—4,4′,6-Tri-*O*-methylmaesopsin (80 mg) in 4% potassium hydroxide solution (20 ml) was heated for 1 h on a water-bath. After cooling to 0 °C and neutralization (3N-H_2SO_4) the solution was extracted (3 ×) with ether. The ethereal phase was dried (Na_2SO_4) and evaporated. P.l.c. of the residue (benzene–acetone 9 : 1 v/v) gave (±)-3-hydroxy-4,6-dimethoxy-3-(4-methoxybenzyl)benzo[*b*]furan-2(3*H*)-one (38 mg, 49%), R_F 0.37, identical with the product of photolysis (above).

(±)-*Methyl* 2-*Hydroxy*-3-(4-*methoxyphenyl*)-2-(2,4,6-*trimethoxyphenyl*)*propionate* (10).—The benzo[*b*]furan-2(3*H*)-one (9) (20 mg) was methylated with dimethyl sulphate. P.l.c. (benzene–acetone, 85 : 15 v/v) gave an amorphous solid (9 mg, 45%), R_F 0.46, red-brown with the spray reagent (Found: M^+ − 18, 358.143. $C_{20}H_{22}O_6$ requires 358.142); *m/e* 358 (2.1%), 312 (2.0), 255 (31), 195 (46), 167 (36), 149 (100), and 121 (11.3); τ ($CDCl_3$) 3.10 (d, 2′- + 6′-H, *J* 8.0 Hz), 3.30 (d, 3′- + 5′-H, *J* 8.0 Hz), 3.93 (s, 3- + 5-H), 4.27 (s, OH), 6.22, 6.27, and 6.30 (s, 3 × OMe), 6.49 (s, 2 × OMe), and 6.67 (s, CH_2); $\nu_{max.}$ ($CHCl_3$) 1 750 cm^{-1} (carboxylic C=O).

Methylation with diazomethane gives the same product.

4,6-*Dimethoxy*-3-(4-*methoxybenzylidene*)*benzo*[b]*furan*-2-*one* (11).—The 3-hydroxy-3-benzylbenzofuran-2-one (9) (50 mg) in ethanol (20 ml) and 3N-hydrochloric acid (1 ml) were refluxed for 30 min. The solution was neutralized ($NaHCO_3$) and evaporated. The product crystallized as fine yellow needles (48 mg), m.p. 168° (from acetone) (lit.,[1] 167°) (Found: M^+, 312.099; C, 69.2; H, 5.2%. Calc. for $C_{18}H_{16}O_5$: *M*, 312.099; C, 69.2; H, 5.2%); *m/e* 312 (100), 297 (37), and 269 (27); τ ($CDCl_3$) 1.90 (d, 2′- + 6′-H, *J* 8.5 Hz), 2.10 (s, CH), 3.10 (d, 3′- + 5′-H, *J* 8.5 Hz), 3.72 and 3.78 (dd, 5- + 7-H, *J* 2.0 Hz), and 6.10, 6.17, and 6.21 (s, 3 × OMe); $\nu_{max.}$ ($CHCl_3$) 1 785 cm^{-1} (lactone C=O).

Synthesis of 4,6-*Dihydroxy*-3-(4-*hydroxybenzylidene*)*benzo*[b]*furan*-2-*one.*—*p*-Hydroxyphenylpyruvic acid (2.19 g), phloroglucinol (1.5 g) and 3N-hydrochloric acid (1.5 ml) in water (25 ml) were heated on a water-bath for 15 min. The precipitate which settled on cooling was washed with iced water. P.l.c. gave a product, R_F 0.56 in benzene–acetone (6 : 4 v/v), which was isolated as a yellow amorphous *solid* (1.2 g, 40%) (Found: M^+, 270.051. $C_{15}H_{10}O_5$ requires *M*, 270.053); *m/e* 270 (100) and 242 (53); τ [$(CD_3)_2CO$] 0.30, 0.83, and 1.03 (all broad s, 3 × OH), 1.90 (d, 2′- + 6′-H, *J* 8.5 Hz), 2.00 (s, CH), 3.09 (d, 3′- + 5′-H, *J* 8.5 Hz),

[13] F. du R. Volsteedt and D. G. Roux, *Tetrahedron Letters*, 1971, 1647.

[14] R. Tominaga, *J. Pharm. Soc. Japan*, 1953, **73**, 1179.

and 3.72 and 3.79 (dd, 5- + 7-H, J 2.0 Hz), $\nu_{max.}$ ($CHCl_3$) 1 740 cm^{-1} (conj. lactone C=O).

Methylation of the phenol (50 mg) with dimethyl sulphate, followed by p.l.c. (benzene–ethyl acetate, 99 : 1 v/v) gives a product (R_F 0.60) which crystallizes as fine yellow needles (45 mg, 90%), m.p. 168° (from acetone), identical (n.m.r. and mass spectra and mixed m.p.) with 4,6-dimethoxy-3-(4-methoxybenzylidene)benzo[*b*]furan-2-one (above).

4,6-*Di*-O-*acetyl*-3-(4-O-*acetylbenzylidene*)*benzo*[b]*furan*-2-*one*.—The free phenol (174 mg) was acetylated (acetic anhydride–pyridine). P.l.c. (benzene–acetone, 97.5 : 2.5 v/v) gave yellow *needles*, R_F 0.22 (180 mg), m.p. 201° (from methanol–acetone) (Found: M^+, 396.080; C, 63.7; H, 4.1. $C_{21}H_{16}O_8$ requires M, 396.084; C, 63.6; H, 4.1%); *m/e* 396 (10%), 354 (25), 312 (47), 270 (100), and 242 (9.4); τ ($CDCl_3$) 1.90 (d, 2'- + 6'-H, J 8.5 Hz), 2.20 (s, CH), 2.82 (d, 3'- + 5'-H, J 8.5 Hz), 3.10 and 3.19 (dd, 5- + 7-H, J 2.0 Hz), and 7.57, 7.67, and 7.70 (s, 3 × OAc).

Irradiation of 2,4,4',6-*Tetra*-O-*methylmaesopsin in Ethanol*.—Tetra-*O*-methylmaesopsin (100 mg) in ethanol (100 ml) was irradiated at 350 nm for 4 h under nitrogen. Removal of the solvent and p.l.c. (benzene–acetone, 9 : 1 v/v) gave a solid, R_F 0.67. This was shown by further p.l.c. to consist of two compounds, R_F 0.60 and 0.50 (in benzene–acetone, 96 : 4 v/v).

2-*Ethoxy*-2'-*hydroxy*-2,4',6'-*trimethoxy*-3-(4-*methoxyphenyl*)*propiophenone* (12).—The acetal (12) (26 mg, 26%), R_F 0.50, was obtained as an amorphous *solid* (Found: $M^+ - 31$, 359.151. $C_{20}H_{23}O_6$ requires 359.149); *m/e* 359 (11.6%), 358 (10.7), 345 (10.2), 344 (9.6), 329 (12.3), 313 (21), 269 (41), 209 (96), 181 (81), 163 (5.1), and 121 (100); τ ($CDCl_3$) −1.20 (s, OH), 2.87 (d, 2- + 6-H, J 8.5 Hz), 3.25 (d, 3- + 5-H, J 8.5 Hz), 3.92 and 4.02 (dd, 3'- + 5'-H, J 2.0 Hz), 6.15, 6.22, and 6.27 (all s, 3 × OMe), 6.47 (q, OCH_2), 6.62 (s, CH_2), 6.72 (s, OMe), and 8.89 (t, CH_3).

The fraction R_F 0.60 was 2'-hydroxy-α,4,4',6'-tetramethoxy-*cis*-chalcone.[7]

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