Photochemical Deoxygenation of an α-Ketol: The Dihydroflavonol–Flavanone Conversion

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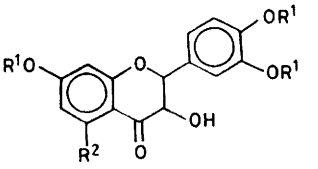
Irradiation of optically pure 2,3-*trans*-3-hydroxyflavanones in anhydrous ethyl acetate leads directly to free phenolic flavanone analogues with complete retention of configuration at C(2). Similarly their methyl ethers give the corresponding flavanones and flavones. The reaction represents the photochemical equivalent of a reduction under Clemmensen conditions.

DUE to the purported central role of the chalcone–flavanone pair in flavonoid biogenesis,[1-4] attention has been pre-eminently focused on the introduction of the 3-hydroxy group leading to the generically related 3-hydroxyflavanones, flavan-3,4-diols, and flavan-3-ols. However, with the recent discovery of α-hydroxychalcones [5,6] the reverse process, hitherto achieved only by reduction under modified Clemmensen conditions of 3-hydroxyflavanones to flavanones,[7] assumes greater significance. We now report an interesting photolytic equivalent for such hydrogenolysis, thus providing more convenient access to optically pure free phenolic flavanones.

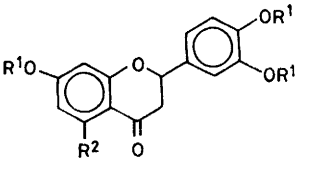
Irradiation of (+)-fustin (1; 2*R*, 3*R*) at 350 nm in dry ethyl acetate gives the flavanone (−)-butin (6; 2*S*) in 17% (37%) † yield. Under similar conditions (+)-3′,4′,7-tri-*O*-methylfustin (2) gives both 2*S*-flavanone (7) [7% (21%) †] and flavone (11) [5% (15%) †] analogues. In the presence of phloroglucinol the yield of the flavanone (6) increases to 28% (47%) † on irradiation of (+)-fustin (1), and those of the flavanone (7) and flavone 11), to 24% (45%) † and 15% (28%),† respectively, in the case of its trimethyl ether (2). However, with naphthalene as a triplet quencher, photolysis of (+)-3′,4′,7-tri-*O*-methylfustin (2) leads to a significant reduction in the yield of the flavanone (7) [1% (7%) †], while that of the flavone (11) increases to 8% (53%).† Complete quenching of the reaction occurs with molecular oxygen. Identical product distribution is obtained with (+)-fustin (1; 2*S*, 3*S*) except for the anticipated inverse configuration (2*R*) of the flavanone (6).

To some extent these results may be rationalized on the simple basis of reduction by the media employed, but for the low overall yields obtained with naphthalene in the same solvent. The latter strongly indicates flavanone formation from the triplet excited state of the dihydroflavonol. This conversion, requiring cleavage of the C(3)–OH bonds, is speculatively regarded as proceeding by the equivalent of a Norrish type II process by β-hydrogen transfer *via* a five-membered cyclic transition state (*cf.* Scheme), the 3-eq-hydroxy favouring the ' in plane *n*-orbital-initiated ' mechanism.[8,9] The increased yields of flavanone and flavone in the presence of phloroglucinol could be due to its role in facilitating rapid hydrogen transfer to the electron-deficient oxygen of the excited states (S_1 and T_1) and thus C(3)–O bond fragmentation.

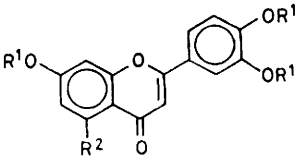
Since prolonged irradiation of the methyl ether of the flavanone (7), as the major product of photolysis, leads to



(1) $R^1 = R^2 = H$
(2) $R^1 = Me$, $R^2 = H$
(3) $R^1 = H$, $R^2 = OH$
(4) $R^1 = Me$, $R^2 = OH$
(5) $R^1 = Me$, $R^2 = OMe$

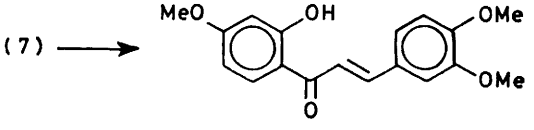


(6) $R^1 = R^2 = H$
(7) $R^1 = Me$; $R^2 = H$
(8) $R^1 = H$, $R^2 = OH$
(9) $R^1 = Me$, $R^2 = OH$
(10) $R^1 = Me$, $R^2 = OMe$



(11) $R^1 = Me$, $R^2 = H$
(12) $R^1 = Me$, $R^2 = OH$
(13) $R^1 = Me$, $R^2 = OMe$

only minor transformation into the flavone (11) [1% (6%) †], it would appear that the intermediacy of the former during flavone formation may be excluded. Assuming, however, the liberation of nascent oxygen during the reaction, an oxidative origin of the flavone

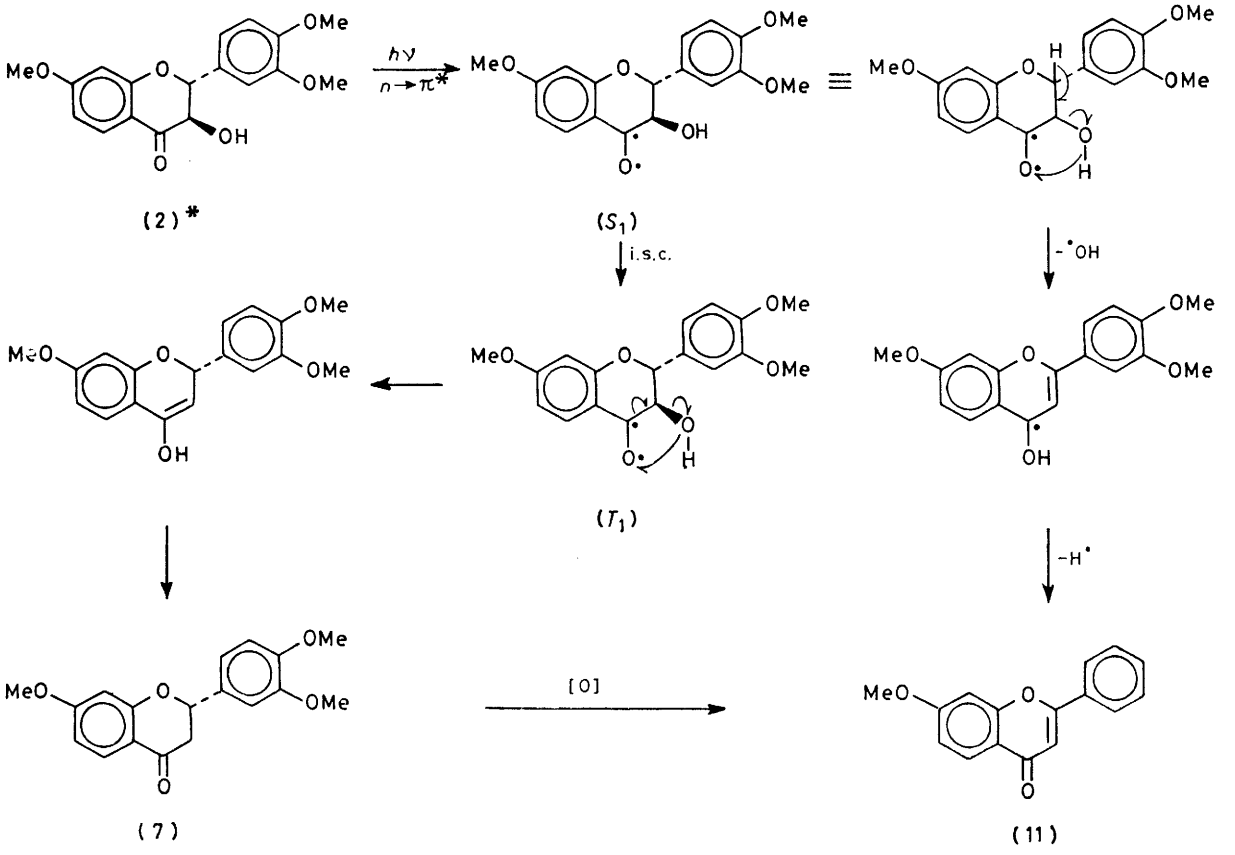


(14)

[*i.e.* (7) ⟶ (11)] might represent a plausible alternative to the proposed route (*cf.* Scheme). The low percentage conversion (*ca.* 9%) of the flavanone (7) into the isomeric

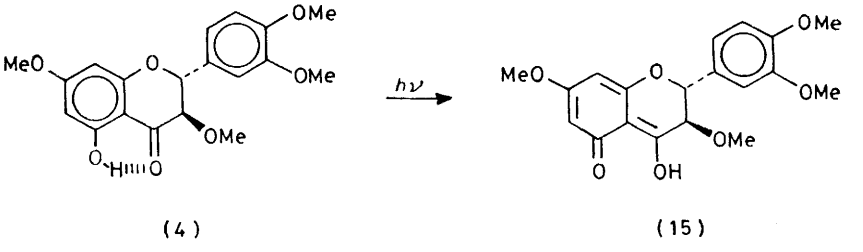
† Percentage conversion based on consumption of starting material.

trans-chalcone (14) obtained under identical conditions is of importance, since equilibration with the chalcone would lead to undesired reduction of the optical purity of the flavanone. This contrasts with our previous observation [10] where photolysis of (±)-3,3',4',7-tetra-*O*-methylfustin in a polar solvent (MeOH) resulted in a *trans*-chalcone ⇌ flavanone equilibrium in favour of the chalcone.



SCHEME * Sequence for 2*R*-enantiomer only

Due to hydrogen transfer from the 5-hydroxy in the excited states as with 3-methoxyflavones [11] (3) ⟶ (15), both (+)-dihydroquercetin (3) and its 3',4',7-trimethyl ether (4) resist transformation under similar conditions.



Irradiation of (+)-3',4',5,7-tetra-*O*-methyldihydroquercetin (5; 2*R*, 3*R*) in the presence of phloroglucinol gives reduced yields of the 2*S*-flavanone (10) [4% (7%) *] As this factor severely hampers the general applicability of the method, a different approach is necessitated.

(+)-3',4',7-Tri-*O*-methyldihydroquercetin (4) irradiated in the presence of benzophenone (0.05M) as triplet sensitizer gives both the flavanone (9) and flavone (12) in

* Percentage conversion based on consumption of starting materials.

equally low proportions (*ca.* 2% each). Under similar conditions addition of phloroglucinol led to an increase in production of the flavanone [7% (23%) *] while that of the flavone remained constant.

The constitution of products derived from (+)-3′,4′,7-tri-*O*-methylfustin (2) was confirmed by synthesis and subsequent n.m.r. comparison. Equilibration of the *trans*-chalcone (14) with sodium acetate [12] gave the flavanone (7) (54%), which was dehydrogenated with DDQ [13] to the flavone (11) (70%) in good yield.

Considering the difficulties encountered in the Clemmensen-type of reduction of 3-hydroxyflavanones to flavanones,[14] leading to modification of reaction conditions for resorcinol-based analogues,[15] the above photochemical deoxygenation furnishes a general method of direct access to optically pure flavanones in moderate yield.

EXPERIMENTAL

Irradiation of compounds in anhydrous ethyl acetate in a quartz vessel was carried out in a slow current of nitrogen (*ca.* 1 ml min^{-1}) in a Rayonet photochemical reactor at 350 nm. T.l.c. was performed on DC–Plastikfolien Kieselgel 60 F_{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. 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. M.p.s were determined with a Reichert hot-stage apparatus. ^1H 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 c.d. data on a JASCO J-20 spectropolarimeter.

Irradiation of Fustin and Derivatives.—(i) (+)-*Fustin* (1; 2*R*, 3*R*). (+)-Fustin (200 mg) from *Acacia mearnsii* [16] was irradiated for 9 h, the solvent evaporated, and the mixture separated by p.l.c. with benzene–acetone (7 : 3). Two bands, R_F 0.46 (35 mg; red) and 0.39 (100 mg; dark brown) were obtained. Crystallisation of the former from water afforded (−)-butin (6; 2*S*) as flat plates, m.p. 224—225 °C (lit.,[17] 223—224 °C), M^+ 272 (65%), δ ([$^2H_6$]acetone) 7.61 (d, 5-H, *J* 8.5 Hz), 6.97—6.72 (m, 2′-, 5′-, and 6′-H), 6.48 (dd, 6-H), 6.32 (d, 8-H, *J* 2.5 Hz), 5.31 (dd, 2-H, *J* 4.25 and 11.75 Hz), 2.97 (dd, 3-eq-H, *J* 16.5 and 11.75 Hz), 2.61 (dd, 3-ax-H, *J* 16.5 and 4.25 Hz), $[\theta]_{353}^{MeOH}$ 0, $[\theta]_{327}^{MeOH}$ + 9 727, $[\theta]_{317}^{MeOH}$ 0, $[\theta]_{300}^{MeOH}$ −21 272, $[\theta]_{256}^{MeOH}$ 0, $[\theta]_{225}^{MeOH}$ + 16 181, $[\theta]_{211}^{MeOH}$ 0. The R_F 0.39 band consisted of (+)-fustin, m.p. 210—212 °C (lit.,[16] 209—211 °C), $[\alpha]_D^{25}$ +24.3° for tetra-acetate (*c* 1.6 in tetrachloroethane) (lit.,[13] +24.4°), $[\theta]_{356}^{MeOH}$ 0, $[\theta]_{328}^{MeOH}$ + 8 364, $[\theta]_{310}^{MeOH}$ 0, $[\theta]_{298}^{MeOH}$ − 22 525, $[\theta]_{273}^{MeOH}$ 0, $[\theta]_{265}^{MeOH}$ + 4 515, $[\theta]_{244}^{MeOH}$ + 5 152, $[\theta]_{226}^{MeOH}$ + 20 262, $[\theta]_{207}^{MeOH}$ 0.

Repetition of this reaction but with addition of phloroglucinol (150 mg) gave the flavanone (1) (56 mg) and starting material (72 mg).

(ii) (+)-3′,4′,7-*Tri*-O-*methylfustin* (2; 2*R*, 3*R*). (+)-Tri-*O*-methylfustin (200 mg), obtained from methylation of (+)-fustin with diazomethane, was irradiated for 5 h. Evaporation of solvent followed by p.l.c. [benzene–acetone (19 : 1)] gave three bands: (a) (−)-3′,4′,7-trimethoxyflavanone (7; 2*S*) (14 mg), R_F 0.38 (red brown), m.p. 111—112 °C (from ethanol) (lit.,[17] 114—115 °C), M^+ 314 (58%), with n.m.r. spectrum identical to that of (±)-tri-*O*-methylbutin,[18] $[\theta]_{355}^{MeOH}$ 0, $[\theta]_{327}^{MeOH}$ + 14 394, $[\theta]_{317}^{MeOH}$ 0, $[\theta]_{298}^{MeOH}$ − 35 757, $[\theta]_{252}^{MeOH}$ 0, $[\theta]_{245}^{MeOH}$ + 2 181, $[\theta]_{220}^{MeOH}$ + 26 151, $[\theta]_{204}^{MeOH}$ 0; (b) (+)-3′,4′,7-tri-*O*-methylfustin (2) (130 mg), R_F 0.22 (brown), crystallised from ethanol as fine plates, m.p. 136—137 °C (lit.,[16] 138—140 °C), $[\theta]_{357}^{MeOH}$ 0, $[\theta]_{328}^{MeOH}$ + 10 787, $[\theta]_{318}^{MeOH}$ 0, $[\theta]_{292}^{MeOH}$ − 27 303, $[\theta]_{271}^{MeOH}$ 0, $[\theta]_{253}^{MeOH}$ + 6 333, $[\theta]_{245}^{MeOH}$ + 6 000, $[\theta]_{221}^{MeOH}$ + 19 030, $[\theta]_{208}^{MeOH}$ 0; (c) 3′,4′,7-trimethoxyflavone (11) (10 mg) R_F 0.16 (yellow), crystallised from ethanol as light yellow needles, m.p. 172—173 °C (lit.,[19] 176 °C), M^+ 312 (100%), δ 8.0 (d, 5-H, *J* 8.75 Hz), 7.44 (dd, 6′-H, *J* 8.75 and 2.0 Hz), 7.25 (d, 2′-H, *J* 2.0 Hz), 6.75—7.00 (m, 5′-, 6-, and 8-H), 6.56 (s, 3-H), 3.92 (s, OMe), 3.90 (s, OMe), and 3.88 (s, OMe).

Repetition of this reaction but with addition of phloroglucinol (100 mg) afforded the flavanone (7) (48 mg), the flavone (11) (30 mg) and unconsumed starting material (2) (88 mg).

The latter reaction was repeated in the presence of naphthalene (0.1M). Work-up as above gave the flavanone (2 mg), the flavone (16 mg), and the starting material (170 mg).

(iii) (−)-*Fustin* (1; 2*S*, 3*S*). (−)-Fustin (200 mg) from *Rhus typhina*, treated and worked up as described for (+)-fustin, gave (+)-butin (6; 2*R*), R_F 0.45 (36 mg; red), with n.m.r. and mass spectra identical to that of (−)-butin, $[\theta]_{367}^{MeOH}$ 0, $[\theta]_{327}^{MeOH}$ − 10 030, $[\theta]_{316}^{MeOH}$ 0, $[\theta]_{298}^{MeOH}$ + 21 121, $[\theta]_{259}^{MeOH}$ 0, $[\theta]_{233}^{MeOH}$ − 13 393, $[\theta]_{220}^{MeOH}$ 0, and unconsumed (−)-fustin, R_F 0.37 (97 mg, brown), crystallised from water as fine needles, m.p. 218—220 °C (lit.,[20] 216—218 °C), $[\alpha]_D^{25}$ −27° for tetra-acetate (*c* 0.7 in tetrachloroethane) (lit.,[13] −25.5°), $[\theta]_{355}^{MeOH}$ 0, $[\theta]_{327}^{MeOH}$ − 10 242, $[\theta]_{317}^{MeOH}$ 0, $[\theta]_{298}^{MeOH}$ + 25 758, $[\theta]_{272}^{MeOH}$ 0, $[\theta]_{265}^{MeOH}$ − 5 303, $[\theta]_{245}^{MeOH}$ − 5 303, $[\theta]_{235}^{MeOH}$ − 11 000, $[\theta]_{208}^{MeOH}$ 0.

Irradiation of (+)-*Dihydroquercetin and Derivatives.*—(i) (+)-3′,4′,5,7-*Tetra*-O-*methyldihydroquercetin* (5; 2*R*,3*R*). The (+)-tetra-*O*-methyl ether (200 mg), obtained from methylation of (+)-dihydroquercetin (3) (Senn Chemicals) with diazomethane and phloroglucinol (100 mg) were irradiated for 5 h. Evaporation of solvent followed by p.l.c. [benzene–acetone (8 : 2)] gave three bands: (a) (−)-3′,4′,5,7-tetramethoxyflavanone (10; 2*S*) (8 mg), R_F 0.40 (red brown), crystallised from ethanol as needles, m.p. 169—170 °C, M^+ 344 (38%), δ 6.98—6.69 (m, 2′-, 5′-, and 6′-H), 6.08—6.00 (dd, 6-, and 8-H, *J* 2.0 Hz), 5.28 (dd, 2-H, *J* 11.75 and 4.0 Hz), 2.84 (s, OMe), 3.82 (s, 2 × OMe), 3.75 (s, OMe), 3.03 (dd, 3-eq-H, *J* 17.0 and 11.75 Hz), and 2.70 (dd, 3-ax-H, *J* 17.0 and 4.0 Hz), $[\theta]_{353}^{MeOH}$ 0, $[\theta]_{324}^{MeOH}$ + 8 242, $[\theta]_{307}^{MeOH}$ 0, $[\theta]_{280}^{MeOH}$ − 18 909, $[\theta]_{254}^{MeOH}$ 0, $[\theta]_{243}^{MeOH}$ + 2 909, $[\theta]_{223}^{MeOH}$ 0; (b) (+)-3′,4′,5,7-*tetra*-O-*methyldihydroquercetin* (5) (74 mg), R_F 0.34 (brown), m.p. 165—166 °C (from ethanol) (lit.,[21] 165—168 °C), M^+ 360 (10.5%), δ 7.08—6.70 (m, 2′-, 5′-, and 6′-H), 6.02 (s, 6-, and 8-H), 4.89 (d, 2-H, *J* 12.0 Hz), 4.37 (d, 3-H, *J* 12.0 Hz), 3.85 (s, OMe), 3.84 (s, OMe), 3.83 (s, OMe), and 3.75 (s, OMe), $[\theta]_{354}^{MeOH}$ 0, $[\theta]_{329}^{MeOH}$ + 5 182, $[\theta]_{315}^{MeOH}$ 0, $[\theta]_{287}^{MeOH}$ − 19 636, $[\theta]_{269}^{MeOH}$ 0, $[\theta]_{248}^{MeOH}$ + 4 909, $[\theta]_{233}^{MeOH}$ 0; (c) 3′,4′,5,7-tetramethoxyflavone (13) (54 mg), R_F 0.16 (yellow), m.p. 190—191 °C (from ethanol) (lit.,[22] 189—190°), M^+ 342 (100%), δ 7.38 (dd, 6′-H, *J* 8.0 and 2.0 Hz), 7.20 (d, 2′-H, *J* 2.0 Hz), 6.84 (d, 5′-H, *J* 8.0 Hz),

* Percentage conversion based on consumption of starting material.

6.48 (s, 3-H), 6.47, 6.25 (dd, 6- and 8-H, J 2.0 Hz), 3.89 (s, (s, OMe), 3.88 (s, 2 × OMe), and 3.84 (s, OMe).

(ii) (+)-*Dihydroquercetin* (3). (+)-Dihydroquercetin (200 mg) and benzophenone (0.05M) were irradiated for 24 h, the solvent evaporated, and the mixture separated by p.l.c. [benzene–acetone (7 : 3)]. Two bands were obtained: (a) (−)-3′,4′,5,7-tetrahydroxyflavanone (8; 2*S*) (14 mg), R_F 0.50 (brown), crystallised from acetone as needles, m.p. 268—269 °C (lit.,[14] 269—271 °C), M^+ 288 (51%), δ ([$^2H_6$]-acetone) 7.03—6.75 (m, 2′-, 5′-, and 6′-H), 5.88 (s, 6- and 8-H), 5.30 (dd, 2-H, J 4.25 and 11.75 Hz), 3.13 (dd, 3-eq-H, J 17.0 and 11.75 Hz), and 2.70 (dd, 3-ax-H, J 17.0 and 4.25 Hz), $[\theta]_{365}^{MeOH}$ 0, $[\theta]_{324}^{MeOH}$ + 4 091, $[\theta]_{307}^{MeOH}$ 0, $[\theta]_{286}^{MeOH}$ − 15 242, $[\theta]_{257}^{MeOH}$ 0, $[\theta]_{245}^{MeOH}$ + 1 939, $[\theta]_{228}^{MeOH}$ 0, $[\theta]_{223}^{MeOH}$ + 14 878, $[\theta]_{212}^{MeOH}$ 0; (b) an R_F 0.42 band consisting of unchanged (+)-dihydroquercetin (90 mg), m.p. 241—243 °C (from water) (lit.,[7] 240—242 °C), M^+ 304 (30%), $[\alpha]_D^{25}$ +29.2° for penta-acetate (c 1.8 in tetrachloroethane), $[\theta]_{370}^{MeOH}$ 0, $[\theta]_{326}^{MeOH}$ + 4 909, $[\theta]_{310}^{MeOH}$ 0, $[\theta]_{290}^{MeOH}$ − 15 939, $[\theta]_{272}^{MeOH}$ 0, $[\theta]_{248}^{MeOH}$ + 3 909, $[\theta]_{227}^{MeOH}$ 0.

Under similar conditions but with omission of benzophenone no reaction (t.l.c.) occurred even at 300 and 250 nm.

(iii) (+)-3′,4′,7-*Tri*-O-*methyldihydroquercetin* (4). The tri-*O*-methyl ether (200 mg), obtained from partial methylation with diazomethane and benzophenone (0.05M), were treated as above and separated by p.l.c. [benzene–acetone (19 : 1)] to give three bands: (a) (−)-5-hydroxy-3′,4′,7-trimethoxyflavanone (9; 2*S*) (4 mg), R_F 0.43 (greyish brown), m.p. 149—150 °C (from ethanol) (lit.,[23] 149—151 °C), M^+ 330 (24%), δ 10.52 (s, 5-OH), 7.63—6.69 (m, 2′-, 5′-, and 6′-H), 5.97 (s, 6- and 8-H), 5.28 (dd, 2-H, J 11.75 and 4.25 Hz), 3.87 (s, OMe), 3.84 (s, OMe), 3.75 (s, OMe), 3.09 (dd, 3-eq-H, J 17.0 and 11.75 Hz), and 2.75 (dd, 3-ax-H, J 17.0 and 4.25 Hz), $[\theta]_{361}^{MeOH}$ 0, $[\theta]_{325}^{MeOH}$ + 6 909, $[\theta]_{307}^{MeOH}$ 0, $[\theta]_{286}^{MeOH}$ − 24 545, $[\theta]_{257}^{MeOH}$ 0, $[\theta]_{246}^{MeOH}$ + 2 788, $[\theta]_{235}^{MeOH}$ + 1 545, $[\theta]_{218}^{MeOH}$ + 21 090, $[\theta]_{207}^{MeOH}$ 0; (b) (+)-3′,4′,7-tri-*O*-methyldihydroquercetin (4) (100 mg), R_F 0.21 (greyish brown), m.p. 169—171 °C (from ethanol), M^+ 346 (45%), δ 11.01 (s, 5-OH), 7.06—6.72 (m, 2′-, 5′-, and 6′-H), 6.01, 5.95 (dd, 6- and 8-H, J 2.0 Hz), 4.94 (d, 2-H), J 11.75 Hz), 4.47 (d, 3-H, J 11.75 Hz), 3.86 (s, OMe), 3.83 (s, OMe), and 3.75 (s, OMe), $[\theta]_{371}^{MeOH}$ 0, $[\theta]_{327}^{MeOH}$ + 6 606, $[\theta]_{311}^{MeOH}$ 0, $[\theta]_{288}^{MeOH}$ − 20 363, $[\theta]_{272}^{MeOH}$ 0, $[\theta]_{252}^{MeOH}$ + 4 212, $[\theta]_{240}^{MeOH}$ + 2 030, $[\theta]_{226}^{MeOH}$ + 18 303, $[\theta]_{207}^{MeOH}$ 0; (c) 5-hydroxy-3′,4′,7-trimethoxyflavone (12) (4 mg), R_F 0.30 (yellow), m.p. 161—163 °C (from ethanol) (lit.,[24] 163 °C), M^+ 328 (100%), δ 9.75 (s, 5-OH), 7.44 (dd, 6′-H, J 8.0 and 2.0 Hz), 7.25 (d, 2′-H, J 2.0 Hz), 6.88 (d, 5′-H, J 8.0 Hz), 6.50 (s, 3-H), 6.40, 6.28 (dd, 6- and 8-H, J 2.0 Hz), 3.91 (s, OMe), 3.90 (s, OMe) and 3.82 (s, OMe).

Repetition of the reaction but with addition of phloroglucinol (100 mg) afforded the flavanone (32 mg), the flavone (4 mg), and the starting material (56 mg). Under similar conditions in absence of benzophenone, no reaction (t.l.c.) occurred even at 300 and 250 nm.

Irradiation of (−)-3′,4′,7-*Trimethoxyflavanone* (7).—The trimethyl ether (200 mg) was irradiated for 24 h, the solvent evaporated, and the mixture separated by p.l.c. [benzene–acetone (24 : 1)] to give three bands: (a) 2′-hydroxy-3,4,4′-trimethoxy-*trans*-chalcone (14) (18 mg), R_F 0.54 (red-brown), crystallised from ethanol as yellow plates, m.p. 151—152 °C (lit.,[25] 156—158 °C), with n.m.r. and mass spectra identical to that of a synthetic sample; (b) (−)-3′,4′,7-trimethoxyflavanone (7) (166 mg), R_F 0.33; (c) 3′,4′,7-trimethoxyflavone (11) (2 mg), R_F 0.08.

Synthesis of (±)-3′,4′,7-*Trimethoxyflavanone* (7) *and* 3′,4′,7-*Trimethoxyflavone* (11).—2′-Hydroxy-3,4,4′-trimethoxy-*trans*-chalcone (14) (1.2 g) in ethanol (100 ml) and sodium acetate (500 mg) in water (10 ml) were refluxed for 2.5 h. Extraction with ether (3 × 100 ml) followed by p.l.c. [benzene–acetone (24 : 1)] afforded racemic flavanone (7) (650 mg), R_F 0.38, with n.m.r. spectrum identical to that of the 2*S*-form obtained from photolysis of tri-*O*-methylfustin as well as starting material (428 mg), R_F 0.47.

The flavanone (100 mg) was dissolved in anhydrous benzene (150 ml), DDQ (100 mg) was added, and the mixture refluxed for 24 h. The solvent was evaporated and the mixture separated by p.l.c. [benzene–acetone (19 : 1)] to give 3′,4′,7-trimethoxyflavone (11) (42 mg), R_F 0.16, and starting material (41 mg).

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