Isolation and Structure Determination of γ-Pyrufuran, A Third Induced Antifungal Dibenzofuran from the Wood of *Pyrus communis* L. infected with *Chondrostereum purpureum* (Pers. ex Fr.) Pouzar

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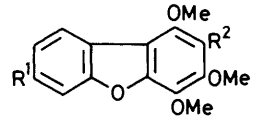
The induced antifungal compound γ-pyrufuran has been isolated from the wood of perry pear trees [*Pyrus communis* L. (Rosaceae) cv. Thorn.] infected with *Chondrostereum purpureum* (Pers. ex Fr.) Pouzar. Spectroscopic and chemical evidence indicate that the compound is one of four 1,2,3,4,7-substituted trimethoxydibenzofurandiols in which one hydroxy group occupies the 7-position. Selective reduction of the dimesylated derivative by hydrogen with a Pd–C catalyst, followed by base-catalysed hydrolysis, produced α-pyrufuran (1,3,4-trimethoxydibenzofuran-2-ol) (**6**), and shows γ-pyrufuran to be 1,3,4-trimethoxydibenzofuran-2,7-diol (**1**).

We have previously reported[1] the occurrence of two dibenzofuran phytoalexins, α- and β-pyrufuran, in the wood of perry pear (*Pyrus communis* L.) infected with *Chondrostereum purpureum*, the fungus that causes silver leaf disease. These compounds were found to accumulate in a narrow, darkly pigmented interface between the healthy and infected tissue. We now report the isolation and identification of a third dibenzofuran phytoalexin, γ-pyrufuran (**1**), from the same source.

γ-Pyrufuran (**1**) was isolated by adsorption chromatography from ethanolic extracts of wood of perry pear which contained infections of *C. purpureum*.

The mass spectrum of the pure, non-crystalline γ-pyrufuran gave a molecular ion $[C_{15}H_{14}O_6]^{+\cdot}$ and a base peak $[M - Me]^+$, $[C_{14}H_{11}O_6]^+$. Chemical ionisation (methane) produced an $[M + H]^+$ ion, *m/z* 291. The ^{1}H n.m.r. spectrum showed peaks assignable to three methoxy groups [δ 3.95, 3.97, and 4.09 (each 3 H, s)], three aromatic protons, the coupling constants of which indicated that they probably occurred in a 1,2,4-substituted benzene ring [δ 6.83 (1 H, dd, *J* 8.0 and 2.0 Hz), 7.01 (1 H, d, *J* 2.0 Hz), 7.74 (1 H, d, *J* 8.0 Hz)], and two replaceable protons [δ 5.87 (2 H, s)]. The two replaceable protons were shown to be assignable to hydroxy groups by (i) methylation (diazomethane) which produced a pentamethoxy product [δ_H 3.84, 3.92, 3.95, 4.01, and 4.10 (each 3 H, s)] of molecular ion $[C_{17}H_{18}O_6]^{+\cdot}$, and (ii) acetylation (acetic anhydride–pyridine) which produced a diacetate [δ_H 2.31, and 2.38 (each 3 H, s)] containing three methoxy groups [δ_H 3.93, 3.95, and 4.12 (each 3 H, s)], and possessing a molecular ion $[C_{19}H_{18}O_8]^{+\cdot}$. The i.r. spectrum of γ-pyrufuran supported these observations, absorption bands being assignable to the same functional groups; OH (3 590w, 3 520m, and 3 320m, br cm^{-1}), aromatic (3 020w, 3 000w, 1 617m, and 1 515m), CH_3 (2 935m and 2 830w), and C–O (1 060s and 1 036s). There was no signal assignable to carbonyl.

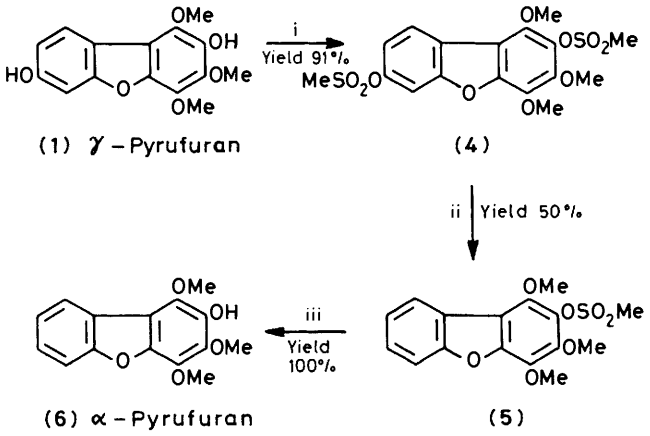
From this information it was deduced that γ-pyrufuran was a dihydroxytrimethoxy substituted derivative of a $C_{12}H_8O$ parent compound in which the oxygen atom existed as an ether linkage. The u.v. spectrum of γ-pyrufuran displayed absorption maxima at $\lambda_{max.}$(log ε) 210 (4.41), 227 (4.43), 262 (4.19), and 297 nm (4.20), a pattern characteristic of dibenzofurans.[1,2] In the aromatic region of the ^{1}H n.m.r. spectrum of γ-pyrufuran, the signal at δ 7.74 (*J* 8.0 Hz) was observed to be *ortho*-coupled to the signal at δ 6.83 (*J* 8.0 and 2.0 Hz) which was, in turn, *meta*-coupled to the remaining signal at δ 7.01 (*J* 2.0 Hz). Consequently, if γ-pyrufuran was a dibenzofuran it would be 1,2,3,4,7- or 1,2,3,4,8-substituted. The n.m.r. signals of protons at positions 1 and 9 in dibenzofurans occur at low field, often at



	R^1	R^2
(1)	OH	OH
(2)	OMe	OMe
(3)	OAc	OAc
(4)	OSO_2Me	OSO_2Me
(5)	H	OSO_2Me
(6)	H	OH

δ 7.7—8.1 unless *ortho*- or *para*-substituents are present.[1-4] The signal at δ 7.74 was therefore assigned to position 9, and it followed from the ^{1}H n.m.r. interpretation that γ-pyrufuran was a 1,2,3,4,7-substituted dibenzofuran. This was supported by comparison of the ^{1}H n.m.r. spectrum of methylated γ-pyrufuran with that of 2,7-dimethoxydibenzofuran.[5] Methylated γ-pyrufuran produced signals in the aromatic region at δ 7.83 (d, *J* 8.2 Hz), 7.02 (d, *J* 2.2 Hz), and 6.87 (dd, *J* 8.2 and 2.2 Hz). These were comparable with those observed for the 7-substituted ring in 2,7-dimethoxydibenzofuran [δ_H 7.75 (dd, *J* 8.5 and 0.6 Hz, 9-H), 7.02 (dd, *J* 2.2 and 0.6 Hz, 6-H), 6.92 (dd, *J* 8.5 and 2.2 Hz, 8-H)] and differed substantially from those signals observed for the 2-substituted benzene ring [δ_H 7.41 (dd, *J* 9.0 and 0.6 Hz, 4-H), 7.30 (dd, *J* 2.4 and 0.6 Hz, 1-H), 6.94 (dd, *J* 9.0 and 2.4 Hz, 3-H)]. 2,7-Dimethoxydibenzofuran was considered to be a reliable model since the substituents of one ring in a dibenzofuran have only a small influence on the chemical shifts of the n.m.r. signals of the protons in the second ring.[1-3] By the corollary of this argument, the relatively large changes in shifts observed in the aromatic signals on acetylation (+0.28, 6-H; +0.20, 8-H; and +0.18 p.p.m., 9-H) and mesylation (+0.50, 6-H; +0.44, 8-H; and +0.24 p.p.m., 9-H) of γ-pyrufuran indicated that one of the hydroxy groups was located at the 7-position.

That γ-pyrufuran was a dibenzofuran was now confirmed, and the positions of the second hydroxy group determined by a selective reduction of γ-pyrufuran to α-pyrufuran (**6**). This was achieved by a modification of the method described by Clauss and Jenson[6] to remove phenolic hydroxy groups (Scheme). Reaction of γ-pyrufuran with excess of methanesulphonyl chloride in pyridine produced the corresponding bis(mesyloxy) derivative (**4**), molecular ion $[C_{17}H_{18}O_{10}S_2]^{+\cdot}$. Attempts to reduce this with hydrogen and 10% palladium on charcoal failed when a trimethylamine scavenger in refluxing methanol was used; however, a selective reduction took place giving a 50%



Scheme. Selective reduction of γ-pyrufuran. *Reagents:* i, $MeSO_2Cl$, pyridine, 80 °C, 0.5 h; ii, H_2, 10% Pd–C, Et_3N, reflux for 2 h; iii, KOH, 80% 1,4-dioxane–H_2O, reflux for 1 h

yield after 2 h when excess of triethylamine was used without methanol. The product, the monomesyloxy derivative (**5**), molecular ion $[C_{16}H_{16}O_7S]^{+\cdot}$, gave multiplet ^1H n.m.r. signals at δ 7.20—7.60 and 7.89—8.10, comparable to those of dibenzofuran,[3] and is therefore 1,2,3,4-substituted.[1] Reduction had taken place at the 7-position, but the remaining mesyloxy group is protected, probably by steric effects. Base-catalysed hydrolysis of this product produced the corresponding 1,2,3,4-substituted trimethoxydibenzofuranol which was indistinguishable from α-pyrufuran (1,3,4-trimethoxydibenzofuran-2-ol) (**6**) by mass, ^1H n.m.r., i.r., and u.v. spectroscopy or by g.l.c. and t.l.c. characteristics.[1] The second hydroxy group in γ-pyrufuran therefore occupied the 2-position and the molecular structure of γ-pyrufuran was shown to be 1,3,4-trimethoxydibenzofuran-2,7-diol (**1**).

γ-Pyrufuran is the third induced antifungal dibenzofuran to be identified from infected perry pear wood. Like α- and β-pyrufurans, it accumulates in concentrations of 5 000 μg g^{-1} or more at the darkly pigmented interface between healthy and infected tissue. In molecular structure, it differs from α-pyrufuran only by an additional hydroxy group at the 7-position. Dibenzofuran is oxidised by bacteria and fungi to the 2- and 3-hydroxylated dibenzofurans.[7] γ-Pyrufuran might therefore be a fungal metabolite of α-pyrufuran. However, preliminary experiments indicate that (i) α-, β-, and γ-pyrufurans also accumulate in the wood as a result of wounding, and (ii) no γ-pyrufuran was detected in *vitro* liquid cultures of *Chondrostereum purpureum* containing α-pyrufuran. This would suggest that γ-pyrufuran is of host origin and is consequently a phytoalexin.

The stability of aryl methanesulphonate esters to strong oxidising, strong acidic, and moderate basic conditions has previously been demonstrated,[8] and the mechanism and kinetics of their base-catalysed hydrolysis have been investigated.[9] These properties have been put to good use in the protection of phenolic and heterocyclic hydroxy groups during a number of chemical reactions,[8,10–13] including Ullmann condensations.[14] That mesyloxy groups may also be selectively reduced, as demonstrated in the current work, shows additional versatility of this group as a tool in chemical synthesis.

Experimental

All isolated and synthesised compounds were shown to be pure by both t.l.c. and g.l.c. Accurate molecular masses were determined using a Kratos MS 950 mass spectrometer with electron impact ionisation. Chemical ionisation (c.i.) (methane *ca.* 0.3 Torr) and electron impact (e.i.) mass spectra were measured from direct insertion probe samples on a Finnigan 4021 MS-DS instrument. 90 MHz ^1H N.m.r. spectra were recorded on a Perkin-Elmer R32 spectrometer. M.p.s were measured on a Köfler block and are uncorrected. 'SilicAR' CC-4 (Mallinckrodt 100 mesh) was used for column chromatography. T.l.c. was carried out on pre-coated Kieselgel 60 F_{254} plates (Merck: 0.25 mm). G.l.c. was carried out on a 1 m × 2 mm i.d. stainless steel column packed with 1% Dexsil 300 on 100—120 mesh Supelcoport, temperature programmed 130—350 °C at 6 ° min^{-1}, injector 250 °C, flame ionisation detector 300 °C, and carrier gas N_2 at 40 ml min^{-1}. Biological activity was detected by a t.l.c. *Cladosporium cucumerinum* bioassay.[15]

Isolation of γ-Pyrufuran.—A log (15 cm diameter × 50 cm) heavily infected with *Chondrostereum purpureum* was cut from a perry pear tree (*Pyrus communis* L. cv. Thorn). The bark and cambium were discarded and samples of tissue containing the darkly pigmented interface between the brown infected wood and the lighter healthy wood were cut away and collected. These samples were cut into thin shavings (60 g) which were soaked in ethanol (1 l) at 20 °C for 5 days. The ethanol extract was decanted off and the solvent removed under reduced pressure (*ca.* 40 °C). The residue was dissolved in chloroform (5 ml) and chromatographed on a column (60 cm × 3 cm i.d.) of Mallinkrodt (SilicAR) CC-4, eluting with chloroform (500 ml) followed by 2% ethanol–chloroform. The antifungal activity of the fractions was monitored by a t.l.c. *Cladosporium cucumerinum* bioassay[15] using a 5% ethanol–chloroform solvent system. The second major fraction of biological activity (R_F 0.40 on the plate bioassay) was collected and further purified by t.l.c. (5% EtOH–$CHCl_3$) to give γ-pyrufuran as an oil. (The first major fraction of biological acitivity, R_F 0.62 on the plate bioassay, was composed of α- and β-pyrufuran.)

γ-Pyrufuran (**1**) (160 mg) [Found: $M^{+\cdot}$, 290.0799. $C_{15}H_{14}O_6$ requires *M*, 290.0790; $(M - Me)^+$, 275.0559. $C_{14}H_{11}O_6$ requires *m/z* 275.0556]; $\lambda_{max.}$(EtOH; 1 cm) 210 [$\log_{10}$ (ε dm^3 mol^{-1} cm^{-1}) 4.41], 227 (4.43), 262 (4.19), 297 (4.20), and 308sh nm (4.10); $\nu_{max.}$($CHCl_3$; 0.1 mm) 3 590w, 3 520m (free OH), 3 320w,br (bonded OH), 3 020w, 3 000w (Ar), 2 935m, 2 830w (CH_3), 1 617m, 1 515m (Ar), 1 455m, 1 443m, 1 410s (Ar and CH_3), 1 333m, 1 280m, 1 137m, 1 100m, 1 060s, and 1 036s cm^{-1} (COH and COC); δ_H (90 MHz; $CDCl_3$; Me_4Si) 3.95, 3.97, 4.09 (each 3 H, s, together 1-, 3-, and 4-OMe), 5.87 (2 H, s, 2- and 7-OH), 6.83 (1 H, dd, *J* 8.0 and 2.0 Hz, 8-H), 7.01 (1 H, d, *J* 2.0 Hz, 6-H), and 7.74 (1 H, d, *J* 8.0 Hz, 9-H); *m/z* (e.i., 40 eV) 291 (20.4%), 290 (M^+, 96.7), 276 (17.3), 275 (100), 260 (13.1), 245 (10.6), 232 (29.1), 231 (10.9), 229 (19.2), 217 (30.0), 189 (15.8), 161 (10.2), 145 (10.3), and 105 (13.8); *m/z* (c.i., methane; 0.3 Torr) 292 (16.9%), 291 ($M + H^+$, 100), 290 (29.2), 276 (23.0), and 261 (30.7); R_F (5% EtOH–$CHCl_3$) 0.40; R_F (2% EtOH–$CHCl_3$) 0.15; R_F [33% $(CH_3)_2CO$–n-C_6H_{14}] 0.20; R_F (30% n-C_6H_{14}–$CHCl_3$) 0.06; R_t 14.7 min.

Methylation of γ-Pyrufuran.—γ-Pyrufuran (**1**) (25 mg) was quantitatively methylated by reaction (24 h, 20 °C) with excess of diazomethane in diethyl ether (5 ml). The product was isolated by t.l.c. (2% EtOH–$CHCl_3$) to give 1,2,3,4,7-*pentamethoxydibenzofuran* (**2**) (26 mg) as an oil [Found: $M^{+\cdot}$, 318.1102. $C_{17}H_{18}O_6$ requires *M*, 318.1103; $(M - Me)^+$ 303.0905. $C_{16}H_{15}O_6$ requires *m/z* 303.0869]; $\lambda_{max.}$(EtOH; 1 cm) 229 (log ε 4.61), 262 (4.32), 292 (4.31), 296sh (4.30), and 308 nm (4.16); $\nu_{max.}$($CHCl_3$; 0.1 mm) 3 020w, 3 000w (Ar), 2 935m, 2 830w (CH_3) 1 603m, 1 500m (Ar), 1 480m, 1 455m, 1 420m, 1 400s (Ar and CH_3), 1 270m, 1 190m, 1 143s, 1 070s, and 1 050s cm^{-1} (COC); δ_H (90 MHz; $CDCl_3$; Me_4Si) 3.84, 3.92, 3.95, 4.01, 4.10 (each 3 H, s, together 1-, 2-, 3-, 4-, and 7-OMe), 6.87 (1 H, dd, *J* 8.2 and 2.2 Hz, 8-H), 7.02 (1 H, d, *J* 2.2 Hz, 6-H), and 7.83

(1 H, d, *J* 8.2 Hz, 9-H); *m/z* (e.i.; 40 eV) 319 (18.7%), 318 (M^+, 100), 304 (14.3), 303 (77.9), 288 (13.8), 273 (15.5), 260 (17.4), 245 (33.1), 244 (6.7), 243 (6.8), 217 (16.7), 215 (6.4), 174 (16.3), 159 (17.7), 149 (27.9), 144 (11.8), 131 (5.6), 118 (11.0), 107 (8.3), and 85 (5.3); R_F (2% EtOH–$CHCl_3$) 0.67; R_F [33% $(CH_3)_2CO$–n-C_6H_{14}] 0.46; R_F (30% n-C_6H_{14}–$CHCl_3$) 0.51; R_t 13.1 min.

Acetylation of γ-Pyrufuran.—γ-Pyrufuran (**1**) (50 mg) was quantitatively acetylated by reaction (20 °C, 24 h) with excess of acetic anhydride (1 ml) in pyridine (NaOH dried, 5 ml). The product was isolated by t.l.c. (2% EtOH–$CHCl_3$) to give 2,7-*diacetoxy*-1,3,4-*trimethoxydibenzofuran* (**3**) (64 mg) as rhombic plates, m.p. 98—99.5 °C (from diethyl ether) {Found: M^+, 374.1001. $C_{19}H_{18}O_8$ requires *M*, 374.1002; [*M* − $(COCH_2)_2$ − Me]$^+$, 275.0551. $C_{14}H_{11}O_6$ requires *m/z* 275.0556}; $\lambda_{max.}$(EtOH; 1 cm) 230 (log ε 4.54), 263 (4.23), 289 (4.18), 300sh (4.12), and 311 nm (3.99); $\nu_{max.}$($CHCl_3$; 0.1 mm) 3 020w, 3 000w (Ar), 2 937m, 2 833w (CH_3), 1 760s (C=O), 1 590m, 1 500m (Ar), 1 477m, 1 453m, 1 422m, 1 403m (Ar and CH_3), 1 368s (COMe), 1 282m, 1 190s, 1 128m, 1 120m, 1 100m, 1 073s, and 1 040s cm^{-1} (COC); δ_H (90 MHz; $CDCl_3$; Me_4Si) 2.31, 2.38 (each 3 H, s, together 2- and 7-OCOMe), 3.93, 3.95, 4.12 (each 3 H, s, together 1-, 3-, and 4-OMe), 7.03 (1 H, dd, *J* 8.2 and 2.0 Hz, 8-H), 7.29 (1 H, d, *J* 2.0 Hz, 6-H), and 7.92 (1 H, d, *J* 8.2 Hz, 9-H); *m/z* (e.i. 40 eV) 375 (6.9%), 374 (M^+, 33.9), 333 (10.6), 332 (56.8), 291 (16.6), 290 (95.1), 289 (13.2), 276 (16.1), 275 (100), 274 (6.0), 260 (7.3), 259 (5.2), 246 (7.2), 232 (16.2), 231 (18.9), 229 (9.5), 217 (13.2), 203 (10.2), 189 (6.8), 160 (8.6), 104 (4.5), and 43 (61.3); R_F (2% EtOH–$CHCl_3$) 0.64; R_F [33% $(CH_3)_2CO$–n-C_6H_{14}] 0.32; R_F (30% n-C_6H_{14}–$CHCl_3$) 0.39; R_t 17.3 min.

Mesylation of γ-Pyrufuran.—γ-Pyrufuran (**1**) (80 mg) was mesylated by reaction (80 °C, 0.5 h) with methanesulphonyl chloride (0.2 ml) in pyridine (NaOH dried; 0.15 ml). The reaction was monitored to completion by t.l.c. (2% EtOH–$CHCl_3$), and the product was extracted with chloroform (100 ml), washed with water (2 × 100 ml), and purified by t.l.c. (2% EtOH–$CHCl_3$) to give 2,7-*bis*(*mesyloxy*)-1,3,4-*trimethoxydibenzofuran* (**4**) (111 mg, 91%) as rhombic plates, m.p. 166—168.5 °C (from diethyl ether) [Found: M^+, 446.0334. $C_{17}H_{18}S_2O_{10}$ requires *M*, 446.0341; [*M* − SO_2Me]$^+$, 367.0474. $C_{16}H_{15}SO_8$ requires *m/z* 367.0488]; $\lambda_{max.}$(EtOH; 1 cm) 219 (log ε 4.59), 229 (4.59), 260 (4.25), and 286 nm (4.29); $\nu_{max.}$($CHCl_3$; 0.1 mm) 3 025w, 3 000w (Ar), 2 935m, 2 837w (CH_3), 1 595m, 1 500m (Ar), 1 455m, 1 420m, 1 401m (Ar and CH_3), 1 370s, 1 178s (OSO_2), 1 094m, 1 073s, 1 037m (COC), and 952s cm^{-1}; δ_H (90 MHz; $CDCl_3$; Me_4Si) 3.19, 3.37 (each 3 H, s, together 2- and 7-OSO_2Me), 4.05, 4.07, 4.16 (each 3 H, s, together 1-, 3-, and 4-OMe), 7.27 (1 H, dd, *J* 8.3 and 2.0 Hz, 8-H), 7.51 (1 H, d, *J* 2.0 Hz, 6-H), and 7.98 (1 H, d, *J* 8.3 Hz, 9-H); *m/z* (e.i.; 40 eV) 446 (M^+, 20.8%), 369 (7.9), 368 (19.5), 367 (100), 324 (6.3), 289 (7.7), 288 (16.5), 274 (6.3), 273 (23.3), 270 (5.0), 259 (7.5), 246 (6.1), 245 (39.3), 230 (6.1), 229 (7.2), 200 (5.3), 159 (9.7), 131 (6.9), and 79 (12.9); R_F (2% EtOH–$CHCl_3$) 0.58; R_F [33% $(CH_3)_2CO$–n-C_6H_{14}] 0.18; R_F (30% n-C_6H_{14}–$CHCl_3$) 0.17; R_t 25.8 min.

Selective Reduction of 2,7-*Bis*(*mesyloxy*)-1,3,4-*trimethoxydibenzofuran* (**4**).—A mixture of 2,7-bis(mesyloxy)-1,3,4-trimethoxydibenzofuran (60 mg), triethylamine (2 ml), and 10% palladium on charcoal (0.05 g) was refluxed (2 h) under hydrogen. The reaction was monitored to completion by t.l.c. [33% $(CH_3)_2CO$ n-C_6H_{14}], and the product was extracted with chloroform (100 ml), washed with water (2 × 100 ml), and purified by t.l.c. [33% $(CH_3)_2CO$–n-C_6H_{14}] to give 2-*mesyloxy*-1,3,4-*trimethoxydibenzofuran* (**5**) (24 mg, 50%) as rhombic plates, m.p. 132.5—134 °C (from diethyl ether) [Found: M^+, 352.0601. $C_{16}H_{16}SO_7$ requires *M*, 352.0617; (M − SO_2Me)$^+$, 273.0779. $C_{15}H_{13}O_5$ requires *m/z* 273.0763]; $\lambda_{max.}$(EtOH; 1 cm) 216 (log ε 4.44), 228 (4.46), 259 (4.04), and 282 nm (4.11); $\nu_{max.}$($CHCl_3$; 0.1 mm) 3 025w, 3 000w (Ar), 2 933m, 2 848w (CH_3), 1 597w, 1 585w, 1 500m (Ar), 1 452m, 1 424m, 1 403s (Ar and CH_3), 1 370s (OSO_2), 1 258m (COC), 1 178s (OSO_2), 1 072s, and 1 037s cm^{-1} (COC); δ_H (90 MHz; $CDCl_3$; Me_4Si) 3.35 (3 H, s, 2-OSO_2Me), 4.02, 4.05, 4.14 (3 H, s, together 1-, 3-, and 4-OMe), 7.20—7.60 (3 H, m, 6-, 7-, and 8-H), and 7.89—8.10 (1 H, m, 9-H); *m/z* (e.i.; 40 eV) 352 (M^+, 23.4%), 274 (17.9), 273 (100), 243 (5.7), 230 (25.4), 215 (25.4), 214 (6.4), 213 (5.3), 187 (17.3), 185 (7.3), 144 (24.0), 88 (11.6), and 79 (6.3); R_F (2% EtOH–$CHCl_3$) 0.63; R_F [33% $(CH_3)_2CO$–n-C_6H_{14}] 0.32; R_F (30% n-C_6H_{14}–$CHCl_3$) 0.41; R_t 16.2 min.

Hydrolysis of 2-*Mesyloxy*-1,3,4-*trimethoxydibenzofuran* (**5**).—2-Mesyloxy-1,3,4-trimethoxydibenzofuran (13 mg) and sodium hydroxide (0.1 g) were refluxed (1 h) in 1,4-dioxane (5 ml) and water (1 ml). The product was acidified with hydrochloric acid (M/10; 50 ml), and extracted with diethyl ether (3 × 50 ml). The extracts were washed with water (3 × 50 ml) and purified by t.l.c. (2% EtOH–$CHCl_3$) to give α-pyrufuran (1,3,4-trimethoxydibenzofuran-2-ol) (**6**) (9.7 mg, 96%), the mass, u.v., i.r., and 90 MHz ^1H n.m.r. spectra and t.l.c. and g.l.c. data of which were identical with those in the literature.[1] A similar yield was obtained when the reaction was repeated using potassium hydroxide in ethanol.

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