Synthesis of 4'-*O*-Methyl- and 4',6-Di-*O*-Methyl-chalaurenol

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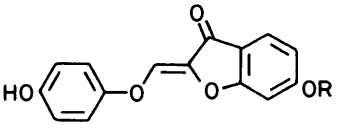
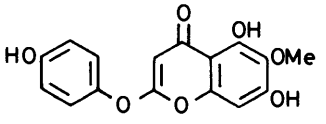
Syntheses are described, of the 4'-*O*- and 4',6-di-*O*-methyl ethers of chalaurenol (**1**), a novel quinol enol ether obtained from peroxidase enzyme oxidation of the important rotenoid and flavonoid precursor, 2',4,4'-trihydroxychalcone. Aryl orthoformate (**12**) was condensed with the enol ethers (**6**) and (**7**), with trimethylsilyl trifluoromethanesulphonate as catalyst, to yield the acetals (**13**) and (**14**), which when heated in pyridine gave the desired ethers (**15**) and (**16**). Hoesch conditions using the aryloxy oxo nitrile (**24**) were unsuccessful, leading to attack at the carbonyl carbon.

Chalaurenol (**1**) is a labile product obtained by an oxidation of 2',4,4'-trihydroxychalcone which fractures the carbon chain and is catalysed by peroxidase enzymes from *Amorpha fruticosa* and other plants, *e.g.* horseradish, garbanzo, and soybean. The preceding paper[1] describes the isolation of chalaurenol and determination of its constitution, including an *X*-ray analysis of 6-*O*-methyl derivative (**2**). The novel product (**1**) is possibly an intermediate in the catabolism of chalcone which is degraded further to form quinol, a widespread natural product found both free and as its monoglucoside. Structure (**1**) may be viewed as a quinol enol ether of a 2-formylcoumaranone, or as an enol ether formed intramolecularly from an aryloxymethyl α-diketone. So far as we are aware, no such structures have been reported previously in nature. The only natural quinol enol ethers known to us are capillarisin (**3**), and a few close relatives,[2]



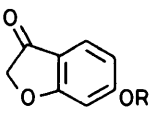
(**1**) R = H
(**2**) R = Me



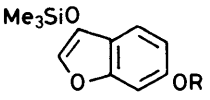
(**3**)

which are ketene acetals. In view of the novelty of structure (**1**) we have investigated synthetic approaches to the system and in this paper we report brief syntheses of the 4'-*O*-methyl ether and 4',6-di-*O*-methyl ether of chalaurenol.

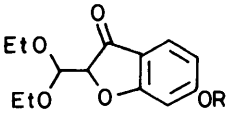
The successful route employed a modern version of the Claisen condensation using as components an orthoester and an enol ether, with catalysis by trimethylsilyl triflate.[3] 6-Methoxycoumaranone (**4**) and 6-hydroxycoumaranone (**5**) were prepared by literature methods[4,5] and converted into the silyl enol ether (**6**) and the bis *O*-trimethylsilyl ether (**7**) by treatment with trimethylsilyl chloride, zinc chloride, and triethylamine. In model condensations, triethyl orthoformate was treated in turn with the enol ethers (**6**) and (**7**) at −78 °C in dichloromethane, employing 5 mol% trimethylsilyl triflate, to yield the diethyl acetals (**8**) (80%) and (**9**) (50%) respectively. Thermal elimination of ethanol from these acetals was accomplished by refluxing in dry pyridine. Treatment of (**8**) in this way gave the desired vinylogous ester (**10**), 30% after 8 h,



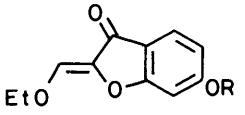
(**4**) R = Me
(**5**) R = H



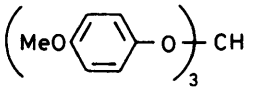
(**6**) R = Me
(**7**) R = $SiMe_3$



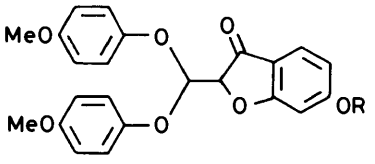
(**8**) R = Me
(**9**) R = H



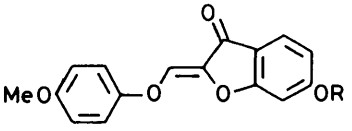
(**10**) R = Me
(**11**) R = H



(**12**)



(**13**) R = Me
(**14**) R = H



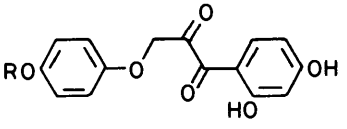
(**15**) R = Me
(**16**) R = H

while its relative (**11**) was obtained from (**9**) in 84% yield after 24 h. The (*Z*)-stereochemistry of (**10**) and (**11**) was inferred by analogy with the chalaurenol series, below.

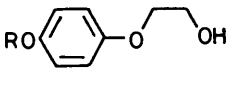
For parallel reactions to reach chalaurenol ethers an aryl orthoformate (**12**) was required. It was found possible, after various trials, to prepare this compound by treating *p*-methoxyphenol with chloroform in aqueous base, though yields were poor (20%). The product, a crystalline solid, was nonetheless unstable and had to be used within a few hours of preparation.

Reaction of the orthoester (**12**) with enol ethers (**6**) and (**7**) was slower than that of triethyl orthoformate but at −50 °C, with 15 mol% catalyst, both acetals (**13**) and (**14**) were obtained

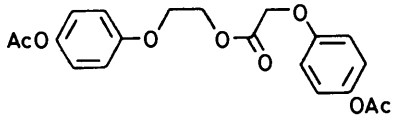
in modest yield (30%). Elimination in refluxing dry pyridine then afforded the desired enol ethers (**15**) and (**16**), 60 and 50% respectively. Repeating the reactions without purification of the intermediate acetals gave chalaurenol 4′-*O*-methyl ether (**15**) and chalaurenol 4′,6-di-*O*-methyl ether (**16**) in improved overall yields (31 and 30% respectively) from the enols (**6**) and (**7**). The ^{1}H n.m.r. and mass spectra of the synthetic ether (**15**) were indistinguishable from those made by permethylation of natural (*Z*)-chalaurenol, thus establishing the geometry of the series. Attempts at the demethylation of (**15**) and (**16**), using boron tribromide or trimethylsilyl iodide, were unsuccessful, and the compounds were too sensitive for transesterification with aryl oxide ions.



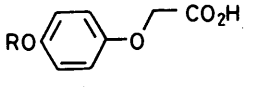
(**17**)



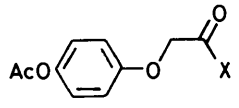
(**18**) R = H
(**19**) R = Ac



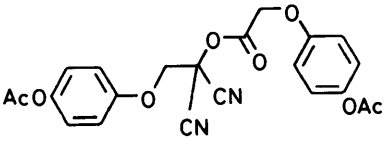
(**20**)



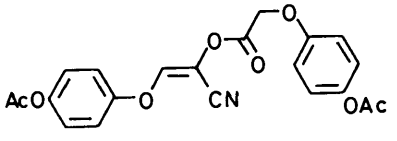
(**21**) R = H
(**22**) R = Ac



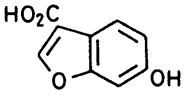
(**23**) X = Cl
(**24**) X = CN



(**25**)



(**26**)



(**27**)

We also investigated an alternative route to chalaurenol and its methyl ethers by way of the diketone (**17**) which it was hoped would cyclise and dehydrate to the desired enol ether. β-Aryloxyethanols (**18**) and (**19**) were prepared and attempts were made to oxidize them to the corresponding aldehydes (on the way to cyanohydrins for Hoesch reactions) but the only product that could be isolated from various Cr^{VI} oxidations of (**19**) was the ester (**20**); presumably oxidation of an intermediate hemiacetal is relatively fast. The aryloxyacetyl chloride (**23**) was readily prepared from the acids (**21**) and (**22**). However, formation of the α-oxo nitrile (**24**) from (**23**) proved unexpectedly difficult. Eventually the conversion was achieved with potassium cyanide and 18-crown-6 in methylene dichloride though the product (**24**) was always contaminated with the dimer (**25**) and its elimination product (**26**). Such dimerisations and eliminations are known reactions of α-oxo nitriles.[6]

On reaction of the unpurified nitrile (**24**) with resorcinol, the desired Hoesch product was not found. The benzofuran (**27**), however, was identified spectroscopically among the products indicating that electrophilic substitution by (**24**) had taken place, at least in part, *via* the carbonyl rather than the nitrile carbon, subsequent elimination and cyclisation occurring.

Experimental

Unless stated otherwise ^{1}H n.m.r. spectra were measured at 90 MHz (continuous wave) in deuteriochloroform using tetramethylsilane as internal standard, and ^{13}C n.m.r. spectra were recorded at 62.9 MHz. Mass spectra were collected using electron impact. 'Drying' of solvents infers the use of anhydrous magnesium sulphate, and 'evaporation' implies reduced pressure operations. Column chromatography refers to the 'dry column' technique, with silica gel.

3,6-*Bis*(*trimethylsiloxy*)*benzofuran* (**7**).—6-Hydroxycoumaranone[4] (5 g), zinc chloride (0.2 g), and triethylamine (15 cm^3) in dry benzene (300 cm^3) were refluxed under nitrogen for 30 min. Trimethylsilyl chloride (9 cm^3) was added dropwise to the mixture which was refluxed for 6 h and then stirred overnight at ambient temperature. The precipitated salt was filtered off and the benzene and excess of triethylamine were distilled off. The residue was distilled to give *compound* (**7**) (8.15 g, 83%), b.p. 110 °C/0.4 mmHg (Found: C, 57.7; H, 7.7%; *m/z* 294.111. $C_{14}H_{22}O_3Si_2$ requires C, 57.1; H, 7.5%; M^+, 294.110); $\delta_H(CCl_4)$ 7.30 (1 H, d, *J* 9 Hz, 4-H), 7.15 (1 H, s, 2-H), 6.85—6.60 (2 H, m, 5- and 7-H), and 0.28 (18, s, 6 × SiMe).

6-*Methoxy*-3-*trimethylsiloxybenzofuran* (**6**).—6-Methoxycoumaranone[5] (5.5 g) was treated as in the preceding experiment but with trimethylsilyl chloride (5 cm^3) only. Product isolation in the same fashion gave *compound* (**6**) (6.5 g, 83%), b.p. 106 °C/0.8 mmHg (Found: C, 60.3; H, 6.7%; *m/z* 236.081. $C_{12}H_{16}O_3Si$ requires C, 61.0; H, 6.8%; M^+, 236.087); δ_H 7.45 (1 H, d, *J* 9 Hz, 4-H), 7.26 (1 H, s, 2-H), 7.00—6.82 (2 H, m, 5- and 7-H), 3.86 (3 H, s, OMe), and 0.28 (9 H, s, 3 × SiMe).

2-(*Diethoxymethyl*)-6-*hydroxycoumaran*-3-*one* (**9**).—The bis(trimethylsiloxy)benzofuran (**7**) (2.2 g) and triethyl orthoformate (1.5 cm^3) in dry dichloromethane (50 cm^3), under nitrogen, were cooled to −78 °C and trimethylsilyl trifluoromethanesulphonate (trimethylsilyl triflate) (60 mm^3) was added. The reaction mixture was stirred at −78 °C for 8 h when it was quenched with water before being allowed to warm to room temperature. The mixture was extracted with dichloromethane (2 × 50 cm^3). The extracts were washed with aqueous sodium hydrogen carbonate (50 cm^3), dried, and evaporated. The residue crystallised from ether–hexane to give the *acetal* (**9**) (0.9 g, 48%), m.p. 114—115 °C [Found: C, 61.7; H, 6.4%; *m/z* 207.063. $C_{13}H_{16}O_5$ requires C, 61.9; H, 6.4%; $(M - OEt)^+$, 207.066]; $\lambda_{max.}$(EtOH) 235 (4.02), 273 (4.10), and 317 nm (4.02); $\nu_{max.}$(KBr) 3 200, 1 680, and 1 610 cm^{-1}; $\delta_H(CDCl_3)$ 8.10 (1 H, s, OH), 7.61 (1 H, d, *J* 9 Hz, 4-H), 6.88—6.60 (2 H, m, 5- and 7-H), 4.97 (1 H, d, *J* 2 Hz, 2-H), 4.77 (1 H, d, *J* 2 Hz, 8-H), 4.02—3.48 (4 H, m, 2 × OCH_2), 1.32 (3 H, t, *J* 7 Hz, Me), and 1.10 (3 H, t, *J* 7 Hz, Me).

2-(*Diethoxymethyl*)-6-*methoxycoumaran*-3-*one* (**8**).—The enol ether (**6**) (2.2 g) was mixed with triethyl orthoformate (2 cm^3) in dry dichloromethane (50 cm^3), and the mixture was cooled under nitrogen to −78 °C. Trimethylsilyl triflate (80 cm^3) was added and the mixture warmed to −50 °C and maintained at this temperature with stirring for 6 h. Quenching with aqueous sodium hydrogen carbonate (50 cm^3) and product isolation as in the preceding experiment gave the *acetal* (**8**) (2.0 g, 80%) as a yellowish oil [Found: *m/z* 221.081. $C_{14}H_{18}O_5$ requires $(M - OEt)^+$, 221.081]; $\nu_{max.}(CHCl_3)$ 1 705, 1 610, and 1 600 cm^{-1}; $\delta_H(CD_3COCD_3)$ 7.50 (1 H, d, *J* 9 Hz, 4-H), 6.78—

6.60 (2 H, m, 5- and 7-H), 4.86 (1 H, d, *J* 2 Hz, 2-H), 4.72 (1 H, d, *J* 2 Hz, 8-H), 3.94 (3 H, s, OMe), 3.90—3.40 (4 H, m, 2 × OCH_2), 1.68 (3 H, t, *J* 7 Hz, Me), and 1.50 (3 H, t, *J* 7 Hz, Me).

2-*Ethoxymethylene*-6-*hydroxycoumaran*-3-*one* (**11**).—The acetal (**9**) (100 mg) was refluxed in dry pyridine (10 cm^3) under nitrogen for 24 h. The solvent was evaporated, and the residue chromatographed on a silica column using chloroform–ether (3:2) as eluant. The major product was the *ethoxymethylene ketone* (**11**) (69 mg, 84%), m.p. 173—174 °C (decomp.) (from dichloromethane–hexane) (Found: C, 63.7; H, 5.2%; *m/z* 206.057. $C_{11}H_{10}O_4$ requires C, 64.1; H, 4.9%; M^+, 206.058); $\lambda_{max.}$(EtOH) 232 (4.10) and 312 nm (4.46); $\nu_{max.}$(KBr) 3 100, 1 690, 1 630, and 1 570 cm^{-1}; δ_H(CD_3COCD_3), 8.05 (1 H, s, 6-OH), 7.60 (1 H, d, *J* 9 Hz, 4-H), 7.14 (1 H, s, 8-H), 6.9—6.65 (2 H, m, 5- and 7-H), 4.35 (2 H, q, *J* 7 Hz, CH_2), and 1.40 (3 H, t, *J* 7 Hz, Me).

2-*Ethoxymethylene*-6-*methoxycoumaran*-3-*one* (**10**).—The acetal (**8**) (0.5 g) was refluxed in dry pyridine (25 cm^3) for 8 h. Product isolation as above, with chromatography on silica and chloroform elution, gave the *enone* (**10**) (120 mg, 30%), m.p. 105 °C (from ether–hexane) (Found: *m/z* 220.073. $C_{12}H_{12}O_4$ requires *M*, 220.074); $\lambda_{max.}$(EtOH), 234 (3.97), 271 (4.06), and 312 nm (4.05); $\nu_{max.}$($CHCl_3$) 1 700 and 1 610 cm^{-1}; δ_H($CDCl_3$) 7.70 (1 H, d, *J* 9 Hz, 4-H), 7.08 (1 H, s, 8-H), 6.85—6.68 (2 H, m, 5-and 7-H), 4.26 (2 H, q, *J* 7 Hz, CH_2), 3.90 (3 H, s, 6-OMe), and 1.44 (3 H, t, *J* 7 Hz, Me).

Tris(p-*Methoxyphenyl*) *Orthoformate* (**12**).—*p*-Methoxyphenol (25 g) and sodium hydroxide (45 g) were dissolved in dioxane (100 cm^3) and water (50 cm^3). Chloroform (12 cm^3) was added slowly to the stirred mixture. After the initial vigorous reaction the mixture was refluxed for 3 h. The cooled product was diluted with water (800 cm^3) and extracted with ether. The extracts were washed, dried, and evaporated. The residue, after treatment with decolourising charcoal in hexane, gave the desired *orthoformate* (**12**) (4.4 g, 17%), m.p. 64—65 °C (lit.,[7] m.p. 50—51 °C) (Found: C, 68.8; H, 6.1%; *m/z* 382.142. Calc. for $C_{22}H_{22}O_6$ C, 69.1; H, 5.8%; M^+, 382.142).

6-*Hydroxy*-2-*Bis*(p-*methoxyphenoxy*)*methylcoumaran*-3-*one* (**14**).—The bis(silyloxy)benzofuran (**7**) (1.1 g) and tris(*p*-methoxyphenyl) orthoformate (1.4 g) in dichloromethane (25 cm^3) were cooled to −78 °C under nitrogen, and trimethylsilyl triflate (0.1 cm^3) was added. The mixture was warmed to −50 °C and stirred at −50 °C for 6 h, when it was quenched with aqueous sodium hydrogen carbonate (25 cm^3). The product was extracted with dichloromethane. The extracts were washed, dried, and evaporated. The residue, an orange oil, was purified by preparative reverse phase h.p.l.c. using a C_{18} column with 70% aqueous methanol as eluant, to yield the *acetal* (**14**) (0.43 g, 28%), m.p. 106 °C (from ether–hexane) [Found: *m/z* 284.068. $C_{23}H_{20}O_7$ requires (M − $C_7H_8O_2$)$^+$, 284.068]; $\lambda_{max.}$(EtOH) 226 (4.39), 276 (4.30), and 318 nm (4.17); $\nu_{max.}$(KBr) 3 180, 1 680, and 1 600 cm^{-1}; δ_H(250 MHz, CD_3COCD_3) 7.50 (1 H, d, *J* 9 Hz, 4-H), 6.98—6.74 (8 H, m, 4 × d, *J* 9 Hz, 2′-, 2″-, 3′-, 3″-, 5′-, 5″-, 6′-, and 6″-H), 6.69—6.63 (2 H, m, 5- and 7-H), 5.96 (1 H, d, *J* 2.5 Hz, 8-H), 5.05 (1 H, d, *J* 2.5 Hz, 2-H), 3.74 (3 H, s, 4′-OMe), and 3.72 (3 H, s, 4″-OMe); δ_C(CD_3COCD_3) 195.0 (C-3), 176.6 (C-7a), 167.6 (C-6), 156.7 (C-1′, C-1″), 151.3 (C-4′), 151.1 (C-4″), 126.2 (C-4), 120.7 (C-2′, C-6′), 120.6 (C-2″, C-6″), 115.4 (C-3′, C-5′), 115.3 (C-3″, C-5″), 115.0 (C-3a), 112.7 (C-5), 103.3 (C-8), 99.4 (C-7), 85.2 (C-2), and 55.8 (4′-OMe, 4″-OMe).

2-*Bis*(p-*Methoxyphenoxy*)*methyl*-6-*methoxycoumaran*-3-*one* (**13**).—The silyl enol ether (**6**) (1.1 g) was treated with the orthoformate (**12**) (1.8 g), as in the preceding experiment. The products were purified in similar fashion to provide the *acetal* (**13**) (0.6 h, 30%) as an oil (Found: *m/z* 442.135. $C_{24}H_{22}O_7$ requires M^+, 422.136); δ_H (250 MHz, $CDCl_3$) 7.49 (1 H, d, *J* 9 Hz, 4-H), 6.87—6.62 (8 H, 4 × d, 2′-, 2″-, 3′-, 3″-, 5′-, 5″-, 6′-, and 6″-H), 6.59—6.55 (2 H, m, 5- and 7-H), 5.80 (1 H, d, *J* 2.5 Hz, 8-H), 4.87 (1 H, d, *J* 2.5 Hz, 2-H), and 3.79, 3.66, and 3.64 (each 3 H, s, OMe).

4′-O-*Methylchalaurenol* (**16**).—The acetal (**14**) (100 mg) was refluxed in dry pyridine (5 cm^3) under nitrogen for 24 h. The pyridine was evaporated off and the products separated on a silica column using chloroform–ether (4:1) as eluant, to yield 4′-O-*methylchalaurenol* (**16**) (41 mg, 59%), m.p. 218 °C (decomp.) (from ethyl acetate) (Found: C, 67.5; H, 4.35%; *m/z* 284.068. $C_{16}H_{12}O_5$ requires C, 67.6; H, 4.25%; M^+, 284.069); $\lambda_{max.}$(EtOH) 231 (4.33) and 322 nm (4.51); $\nu_{max.}$(KBr) 1 700 and 1 600 cm^{-1}; δ_H(250 MHz, CD_3SOCD_3), 11.10 (1 H, br s, OH), 7.59 (1 H, d, *J* 9 Hz, 4-H), 7.51 (1 H, s, 8-H), 7.29 (2 H, d, *J* 9 Hz, 2′- and 6′H), 6.98 (2 H, d, *J* 9 Hz, 3′- and 5′-H), 6.74—6.69 (2 H, m, 5- and 7-H), and 3.76 (3 H, s, OMe); δ_C(CD_3SOCD_3) 181.1 (C-3), 166.9 (C-7a), 166.0 (C-6), 156.2 (C-1′), 149.9 (C-4′), 136.2 (C-2), 132.3 (C-4), 125.2 (C-8), 117.9 (C-2′, C-6′), 115.0 (C-3′, C-5′), 114.0 (C-3a), 112.8 (C-5), 98.3 (C-7), and 55.5 (4′-OMe).

4′,6-*Di*-O-*methylchalaurenol* (**15**).—The acetal (**13**) (0.35 g) was refluxed in dry pyridine (20 cm^3) for 16 h under nitrogen. Product isolation as in the preceding experiment, using chloroform for column elution, gave 4′,6-*di*-O-*methylchalaurenol* (**15**) (119 mg, 48%), m.p. 124—125 °C (from ether–hexane) (Found: C, 68.5; H, 4.9%; *m/z* 298.086. $C_{17}H_{14}O_5$ requires C, 68.45; H, 4.7%; M^+, 298.084); $\lambda_{max.}$(EtOH) 230 (4.39) and 317 nm (4.65); $\nu_{max.}$(KBr) 1 700, 1 650, and 1 605 cm^{-1}; δ_H(250 MHz, $CDCl_3$) 7.68 (1 H, d, *J* 8 Hz, 4-H), 7.36 (1 H, s, 8-H), 7.14 (2 H, d, *J* 9 Hz, 2′- and 6′-H), 6.91 (2 H, d, *J* 9 Hz, 3′- and 5′-H), 6.78—6.73 (2 H, m, 5- and 7-H), and 3.91 and 3.82 (both 3 H, s, OMe). The ^1H n.m.r. spectrum was identical with that of a sample prepared from natural chalaurenol (preceding paper) by refluxing the natural phenol with an excess f methyl iodide in methanol over silver oxide for 5 h. Both samples also had identical mass spectra, and the same retention times on h.p.l.c.

2-(p-*Acetoxyphenoxy*)*ethanol* (**19**).—Quinol (12 g) and 2-chloroethanol (10 cm^3) were added to sodium hydroxide (17 g) in water (500 cm^3) and the mixture was refluxed for 4 h. The mixture was cooled, acidified, and extracted with ethyl acetate. The extracts was dried and evaporated. Chromatography on silica, using ethyl acetate–hexane (2:1) gave the alcohol (**18**) (8.7 g, 52%), m.p. 92—93 °C (from ether–hexane) (Found: C, 62.6; H, 6.8. Calc. for $C_8H_{10}O_3$: C, 62.3; H, 6.5%). Acetylation using acetic anhydride–sodium hydroxide gave the *alcohol* (**19**) (74%), m.p. 73—74 °C (from ether–hexane) (Found: C, 61.3; H, 6.3. $C_{10}H_{12}O_4$ requires C, 61.4; H, 6.2%); $\nu_{max.}$(KBr) 3 500, 3 375, and 1 750 cm^{-1}; δ_H(CD_3COCD_3) 6.97 and 6.95 (both 2 H, d, *J* 9 Hz, 2-, 3-, 5-, 6-H), 4.05 (2 H, t, CH_2), 3.89 (2 H, t, CH_2OH), 3.87 (1 H, br s, O*H*), and 2.21 (3 H, s, COMe).

Oxidation of 2-(p-*Acetoxyphenoxy*)*ethanol*.—2-(*p*-Acetoxyphenoxy)ethanol (200 mg) in dry dichloromethane (2 cm^3) was added to pyridinium chlorochromate (600 mg) suspended in dichloromethane (2 cm^3), and the mixture was stirred at room temperature for 30 h. Dry ether (20 cm^3) was added and the mixture filtered through silica. Evaporation gave an oil whose spectral data indicated it to be mainly the (unwanted) ester (**20**); *m/z* (f.a.b.) 389 (MH^+), 346 (MH − Ac)$^+$, and 304 (MH − 2 × Ac)$^+$; δ_H(250 MHz, $CDCl_3$) 7.06—6.92 (8 H, 4 × d, *J* 8 Hz, ArH), 4.77 (2 H, s, OCH_2CO), 4.53 (2 H, t, CH_2OCO), 4.24 (2 H, t, $ArOCH_2$), and 2.22 and 2.21 (both 3 H, s, Me); δ_C 169.8—169.3 (3 C, 3 × C=O), 157.0, 156.5 (C-1, C-1′), 146.0, 145.7 (C-4, C-4′), 123.3 (4 C, C-3, C-3′, C-5, C-5′), 115.9 (4 C, C-2, C-2′, C-6, C-6′), 67.1, 66.1, 64.0 (3 × OCH_2), and 20.8 (2 × Me).

(p-*Acetoxyphenoxy)acetyl Chloride* (**23**).—*p*-Hydroxyphenoxyacetic acid, m.p. 155—156 °C, was prepared by the literature method, and acetylated in the standard way, to yield the *p*-acetoxyphenoxyacetic acid, m.p. 162—163 °C. Treatment of the latter with thionyl chloride gave the *acid chloride* (**23**), m.p. 75 °C (Found: *m/z* 228.017. $C_{10}H_9{}^{35}ClO_4$ requires *M*, 228.019); $\nu_{max.}$(KBr) 1 790 and 1 745 cm^{-1}.

Reaction of p-*Acetoxyphenoxyacetyl Chloride with Potassium Cyanide.*—The title acid chloride, from the acid (0.5 g), was refluxed in dichloromethane (5 cm^3) with potassium cyanide (250 mg) and 18-crown-6 (25 mg) for 8 h. The reaction mixture was filtered and evaporated to dryness. Spectroscopic examination revealed a mixture of the oxo nitrile (**24**), dimer (**25**), and the nitrile (**26**): this mixture was very unstable and not amenable to purification. The monomeric α-oxo nitrile (**24**) had *m/z* 219.053 ($C_{11}H_9NO_4$ requires M^+, 219.053); δ_H(CD_3COCD_3) 7.04 (4 H, s, ArH), 5.08 (2 H, s, CH_2), and 2.25 (3 H, s, CH_3). The dimer (**25**) had *m/z* (f.a.b.) 439 (MH^+); δ_H(CD_3COCD_3) 7.13 and 7.04 (8 H, 2 × br s, 2 × ArH), 5.10 and 4.97 (both 2 H, s, CH_2), and 2.22 (6 H, s, 2 × Me). The nitrile (**26**) had *m/z* 411.097 ($C_{21}H_{17}NO_8$ requires M^+, 411.097) and δ_H(CD_3COCD_3) 7.79 (1 H, s, OCH=C), 7.22 (8 H, br, ArH), 5.03 (2 H, s, CH_2), and 2.24 (6 H, s, 2 × Me).

Reaction between p-*Acetoxyphenoxyacetyl Cyanide and Resorcinol.*—Resorcinol (0.2 g) and zinc chloride (0.2 g) were added to dry ether (50 cm^3). A dichloromethane solution of the title nitrile (from the preceding experiment) was added, and hydrogen chloride was bubbled through the mixture for 2 h. The product was set aside for several hours when a red oil separated. After decanting the supernatant solvent layer the residue was refluxed in water for 30 min. The organic products were collected in ether and separated on a silica column using hexane–ethyl acetate–acetic acid (50:50:1). Quinol was obtained as a product, and a white solid with spectral characteristics of 6-hydroxybenzofurancarboxylic acid: MH^+ (c.i.), 179 ($C_9H_6O_4$ requires MH^+ 179); $\nu_{max.}$(KBr) 3 300v br and 1 690 cm^{-1}; δ_H(CD_3COCD_3) 7.32 (1 H, d, *J* 9 Hz, 4-H), 7.09 (1 H, s, 2-H), and 6.90—6.77 (2 H, m, 5- and 7-H); δ_C 160.2, 159.5, 152.0, 139.6, 128.4, 116.2, 114.1, 113.9, and 103.2. Insufficient material for satisfactory purification was obtained.

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