Synthesis of Grevillins, Novel Pyrandione Pigments of Fungi. Biogenetic Interrelationships between Grevillins, Pulvinic Acids, Terphenylquinones and Xylerythrins

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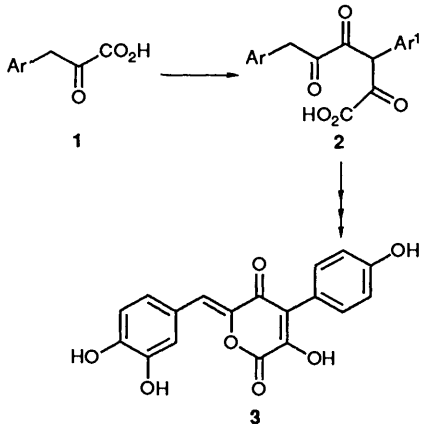
A synthesis of the grevillin group of pyrandione pigments *e.g.* **3**, **23** and **24** present in fungi is described. The synthesis, which is based on a biogenetic model, uses bis-benzylacyloins **9** and their corresponding oxalate derivatives as key intermediates (Scheme 3). Treatment of the grevillins **25–c** with sodium ethoxide in ethanol effects their quantitative isomerisation into the corresponding terphenylquinone pigments **4a–c**. Perkin-type condensations between the terphenylquinones **4** and arylacetic acids in the presence of sodium acetate–acetic anhydride then produces the xylerythrin pigments **29a–e**, whereas rearrangements of **4** in the presence of dimethyl sulphoxide leads to pulvinic acid derivatives, *e.g.* **31**, **32** and **5**. These synthetic studies interrelate the biosynthetic origins of the pigment types **3**, **4**, **5** and **8** together with the related pulvinone **6** and furanone **7** fungal pigments.

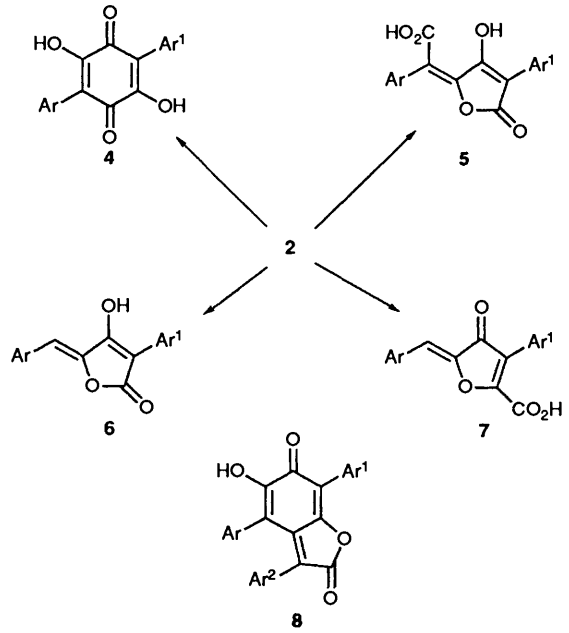
Grevillin is the generic name used to describe the group of orange and red pyrandione pigments *e.g.* **3** which have been isolated from fungi of the genus *Suillus*.[1] The grevillins co-occur with the related terphenylquinones **4** and pulvinic acids **5**, and they have their biogenetic origins in the dimer **2** derived from enzymatic conversion of arylpyruvic acid **1** (Scheme 1).[2] The



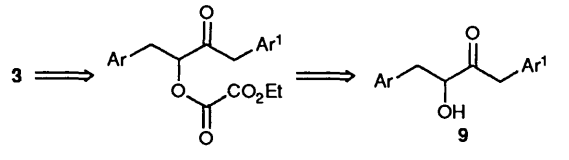
Scheme 1

arylpyruvic acid dimer **2** also serves as the central intermediate in the biosynthesis of the terphenylquinones **4**, the pulvinic acids **5**, in addition to the pulvinone **6**, furanone **7** and xylerythrin **8** families of fungal pigments (Scheme 2).[3] During investigations into the structure, the origins and the biogenetic interrelationships between the fungal pigment types **3–8**, we have earlier described concise syntheses of members of the pulvinone[4] and the pulvinic acid[5] groups of pigments. In continuation of these studies, we now describe a synthetic route to the grevillins **3** using benzylacyloins, *viz.* **9**, as key intermediates (Scheme 3),[6] and illustrate their conversions *in vitro* into terphenylquinones **4** and thence the pulvinic acids **5**, and the xylerythrin group **8** of red quinone methide pigments found in the bark fungus *Peniophora sanguinea*.

Thus, using established methodology,[7] addition of the Grignard reagent derived from 4-methoxybenzyl chloride to the *O*-trimethylsilyl cyanohydrin **10** first led to the unsymmetrically substituted benzylacyloin **11** in 71% yield. Addition of ethyl oxalyl chloride to the benzylacyloin **11** in the presence of

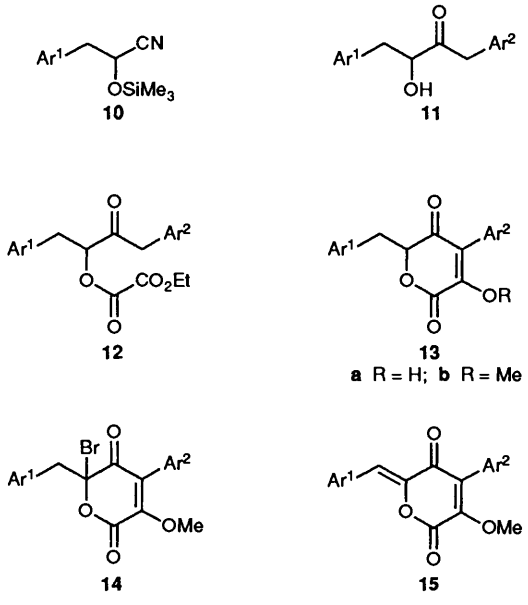


Scheme 2



Scheme 3

triethylamine next led to the corresponding oxalate **12**, which with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in dimethylformamide (DMF) at −15 °C was smoothly converted into the dihydrogrevillin **13a**. The direct oxidation–dehydrogenation of **13a** to the corresponding grevillin proved problematic, *e.g.* 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, Fremy's salt and palladium on charcoal led to recovered starting material or to intractable gums. Methylation of **13a** using diazomethane, however, proceeded smoothly producing the methyl ether **13b**, which when treated with bromine in acetic acid[8] gave the



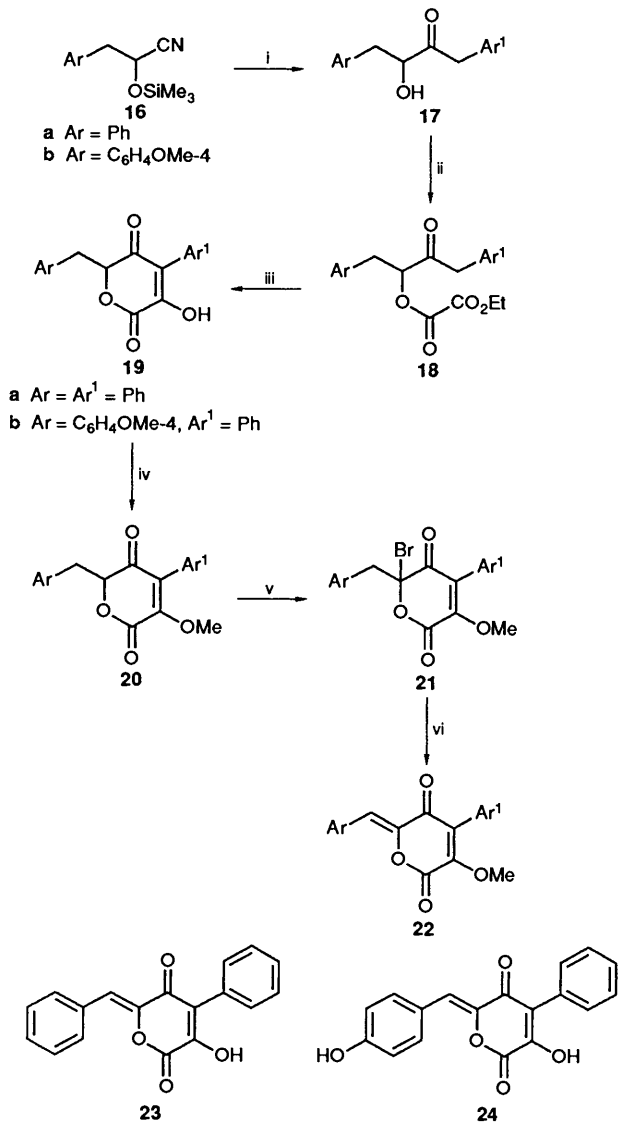
$Ar^1 = C_6H_3(OMe)$-3, 4, $Ar^2 = C_6H_4OMe$-4

bromo derivative **14** in 77% yield. Elimination of the elements of hydrobromic acid from **14** in the presence of DBU, followed by demethylation of the resulting methyl grevillin **15** in the presence of boron tribromide[9] finally produced grevillin B **3** as red crystals which showed spectroscopic data identical with those of natural material produced by the fruiting bodies of *Suillus grevillei*.[10]

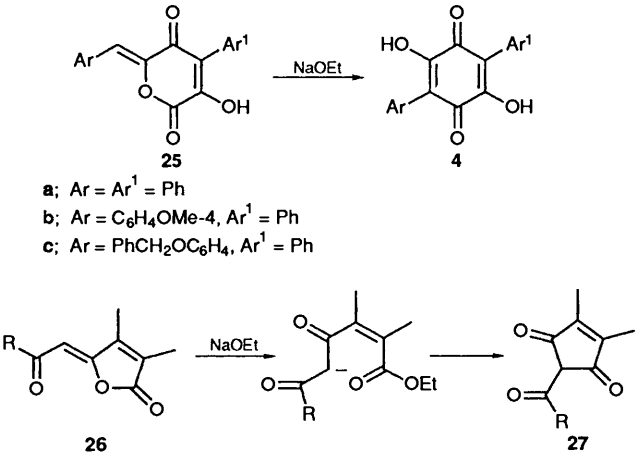
In a similar series of reactions, the cyanohydrins **16a** and **16b** were elaborated to the corresponding grevillins **23** and **24** respectively (Scheme 4).

The isomeric relationships between the grevillin **25** and terphenylquinone **4** structures, which has also been examined by Steglich and co-workers,[11] is formally analogous to the relationship between the ylidenebutenolide and cyclopentenedione structures, *viz.* **26** and **27**, which we have examined in detail.[12] Indeed, this analogy could be fully demonstrated when the grevillin **25** was treated with sodium ethoxide in ethanol. A dense purple precipitate formed almost immediately, and acidification gave the known terphenylquinone **4a**[13] in 90% yield. In a similar manner the synthetic grevillin derivatives **25b** and **25c** could be isomerised in the presence of sodium ethoxide to the terphenylquinones **4b** and **4c** respectively.

Naturally occurring terphenylquinones have previously been linked biogenetically to the xylerythrin **8** and the pulvinic acid **5** families of natural products.[2,3] In our studies we have added further support for this biogenetic link with: (i) the conversion of the terphenylquinones **4a** and **4c** into the corresponding xylerythrins **29a–e** following Perkin reactions with arylacetic acids (to **28**)[14] and demethylation in the presence of hydrobromic acid–acetic acid, and (ii) the conversions of **4a** and **4b** into the pulvinic acids **5a** and **5b**/**5c** respectively *via* the corresponding dilactone intermediates **30a** and **30b**,[15] as outlined in Scheme 5.



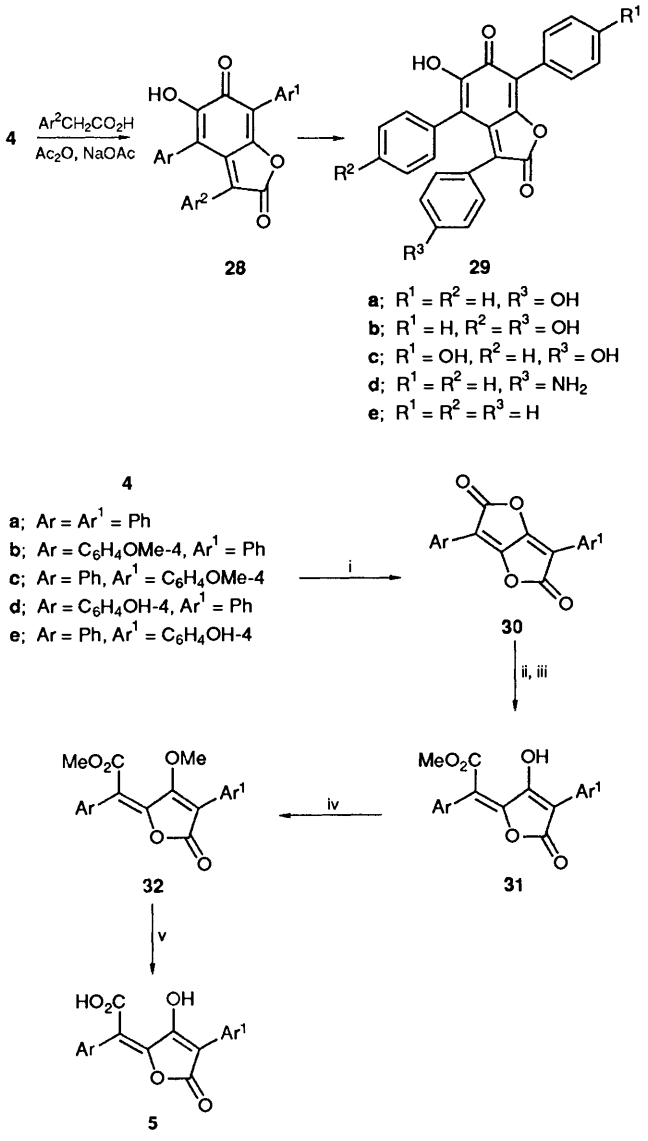
Scheme 4 *Reagents:* i, $PhCH_2MgCl$; ii, $CO_2EtCOCl$, Et_3N; iii, DBU, DMF; iv, CH_2N_2; v, Br_2, AcOH; vi, DBU



Experimental

For general experimental details see ref. 16. For NMR spectroscopic data *J* values are given in Hz. Ether refers to diethyl ether. Light petroleum refers to the fraction boiling in the range 60–80 °C.

3-(3,4-*Dimethoxyphenyl*)-2-*trimethylsilyloxypropanenitrile* **10**.—3,4-Dimethoxyphenylacetaldehyde (5.2 g) was added dropwise onto a stirred mixture of trimethylsilyl cyanide (3.6 cm^3, 1 equiv.)[17] and zinc iodide (1 crystal) at 0 °C under nitrogen. The mixture was stirred for a further 15 min and then distilled to give the title compound (4.85 g, 60%) as a colourless liquid, b.p. 140–145 °C at 2 mmHg, ν_{max}(liquid film)/cm^{-1} 2960m, 2250w, 1595w, 1515m, 1455m, 1425m, 1335w, 1260s, 1240s, 1160s, 1145s, 1105s, 1030s, 920m, 850s, 760m and 730s;



Scheme 5 *Reagents:* i, DMSO, Ac_2O, 100 °C; ii, NaOMe, MeOH; iii, c. HCl; iv, CH_2N_2; v, Me_3SiI

δ_H(no solvent) 0.00 (OTMS), 2.81 (d, *J* 7.0, CH_2), 3.65 (2 × OMe), 4.35 (t, *J* 7.0, CH) and 6.65 (3 × aryl =CH).

4-(3,4-*Dimethoxyphenyl*)-3-*hydroxy*-1-(4-*methoxyphenyl*)-*butan*-2-*one* **11**.—A solution of compound **10** (1 g) in dry ether (10 cm^3) was added dropwise to a solution of 4-methoxybenzylmagnesium chloride (1.5 equiv.) in ether (50 cm^3) heated under reflux in an atmosphere of nitrogen. The mixture was heated under reflux for a further 3 h when a white precipitate formed. The mixture was allowed to cool to room temperature, and then poured onto ice-cooled dilute hydrochloric acid (20 cm^3). The two phase mixture was stirred vigorously at 25 °C overnight. The mixture was extracted with ether (2 × 20 cm^3), and the combined ether extracts were dried and evaporated to leave a solid residue. Column chromatography then gave the title compound (0.84 g, 71%), which recrystallised from light petroleum as white needles, m.p. 81.5–82.5 °C, $\nu_{max}(CHCl_3)$/cm^{-1} 3550w, 2950m, 1720s, 1615s, 1530m, 1475s, 1305m, 1280m, 1160s and 865w; δ_H 2.80 (dd, *J* 6.8 and 14.4, 1 H), 3.10 (dd, *J* 4.7 and 14.4, 1 H), 3.16 (br, OH), 3.72 (CH_2), 3.78 (OMe), 3.83 (OMe), 3.86 (OMe), 4.47 (m, 1 H), 6.62–6.90 (m, 3 × aryl =CH), 6.84 (d, *J* 9.0, 2 × aryl =CH) and 7.04 (d, *J* 9.0, 2 × aryl=CH); δ_C 39.8, 44.9, 55.3, 55.8, 55.9, 76.7, 111.3, 112.5, 114.2, 121.3, 124.9, 128.9, 130.6, 148.1, 149.0, 158.8 and 209.5 (Found: C, 68.5; H, 6.7%; M^+, 330.1471. $C_{19}H_{22}O_5$ requires C, 69.0; H, 6.7%; *M*, 330.1467).

1-(3,4-*Dimethoxyphenyl*)-4-(4-*methoxyphenyl*)-3-*oxobutan*-2-*yl Ethyl Oxalate* **12**.—A solution of compound **11** (550 mg) and triethylamine (224 mm^3, 1 equiv.) in dry tetrahydrofuran (THF) (25 cm^3) was added dropwise to a stirred solution of ethyl oxalyl chloride (235 mm^3, 1 equiv.) in dry THF (25 cm^3) under nitrogen, whereupon a white precipitate formed immediately. The mixture was stirred at 25 °C for 30 min, and then poured onto hydrochloric acid (2 mol dm^{-3}; 30 cm^3). The mixture was extracted with ether (2 × 30 cm^3) and the combined ether extracts were dried and evaporated to leave a crude residue. Column chromatography gave the oxalate (416 mg, 58%) as a colourless oil, ν_{max}(liquid film)/cm^{-1} 2950m, 1770s, 1750s, 1615w, 1515m, 1460m, 1300m, 1250s, 1185s, 1160s, 1030s, 910w, 860w and 760s; δ_H 1.37 (t, *J* 7.2, $CO_2CH_2CH_3$), 3.06 (d, *J* 6.3, CH_2), 3.63 (CH_2), 3.78 (OMe), 3.83 (OMe), 4.36 (q, *J* 7.2, $CO_2CH_2CH_3$), 5.36 (t, *J* 6.3, 1 H), 6.60–6.84 (m, 3 × aryl CH), 6.80 (d, *J* 9.0, 2 × aryl CH) and 7.05 (d, *J* 9.0, 2 × aryl CH); δ_C 13.9, 36.6, 46.1, 55.2, 55.8, 55.9, 63.4, 80.6, 111.2, 112.6, 114.2, 121.6, 124.3, 127.3, 127.3, 130.8, 148.3, 149.0, 156.9, 159.0 and 203.4 (Found: M^+, 4.30.1629; $C_{23}H_{26}O_8$ requires *M*, 430.1627).

6-(3,4-*Dimethoxybenzyl*)-3-*hydroxy*-4-(4-*methoxyphenyl*)-*pyran*-2,5-*dione* **13a**.—A solution of compound **12** (400 mg) in dry dimethylformamide (DMF) (10 cm^3) was added dropwise, over 15 min, to a stirred solution of 1,5-diazabicyclo[5.4.0]undec-5-ene (277 mm^3, 2 equiv.) in dry DMF (10 cm^3) at −15 °C under nitrogen. The resulting orange solution was stirred for 2 h and then poured onto hydrochloric acid (2 mol dm^{-3}; 20 cm^3). The mixture was extracted with ether (2 × 20 cm^3), and the combined extracts were washed with water (3 × 20 cm^3), dried and evaporated to give the crude *dione* (252 mg, 71%) which recrystallised from light petroleum as a cream powder, m.p. 132–135 °C, λ_{max}(EtOH)/nm 234 (ε 17 100), 253 (ε 13 000) and 334 (ε 5900); ν_{max}(KBr)/cm^{-1} 3380br m, 2960w, 1730s, 1665s, 1615s, 1530s, 1475m, 1400w, 1365m, 1270s, 1215s, 1165m, 1035m, 840w and 785w; δ_H 3.33 (d, *J* 4.4, CH_2), 3.73 (OMe), 3.82 (OMe), 3.84 (OMe), 5.31 (t, *J* 4.4, CH), 6.60 (d, *J* 1.9, 1 × aryl =CH), 6.68 (dd, *J* 1.9 and 8.2, 1 × aryl CH), 6.75 (d, *J* 8.2, 1 × aryl =CH), 6.92 (d, *J* 8.9, 2 × aryl =CH) and 7.29 (d, *J* 8.9, 2 × aryl CH); δ_C 40.3, 55.3, 55.8, 55.9, 84.7, 111.2, 112.8, 113.6, 119.8, 121.8, 122.4, 125.9, 131.5, 148.5, 148.9, 160.1, 161.8 and 191.6 (Found: C, 65.4; H, 5.2%; M^+, 384.1198. $C_{21}H_{20}O_7$ requires C, 65.6; H, 5.2%; *M*, 384.1209).

6-(3,4-*Dimethoxybenzyl*)-3-*methoxy*-4-(4-*methoxyphenyl*)-*pyran*-2,5-*dione* **13b**.—An ethereal solution of diazomethane was added to a solution of compound **13a** (240 mg) in ether (10 cm^3) at 0 °C, until the solution remained pale yellow. The mixture was stirred at 0 °C for 5 min, and then evaporated to dryness to leave the *dione* **13b** (243 mg, 97%) which recrystallised from methanol as orange needles, m.p. 107–109 °C, λ_{max}(EtOH)/nm 232 (ε 16 700), 250sh (ε 9040), 271sh (ε 6560) and 329 (ε 3380); $\nu_{max}(CHCl_3)$/cm^{-1} 3400w, 2930m, 1720s, 1670s, 1595s, 1505m, 1445s, 1420m, 1350m, 1285s, 1250s, 1140s, 1025s, 860w, 830w, 805w, 760m and 730m; δ_H 3.30 (m, CH_2), 3.56 (OMe), 3.78 (OMe), 3.82 (OMe), 3.84 (OMe), 5.24 (dd, *J* 4.0 and 4.4, CH), 6.64 (d, *J* 1.9, 1 × aryl =CH), 6.70 (dd, *J* 1.9 and 8.1, 1 × aryl =CH), 6.80 (d, *J* 8.1, 1 × aryl =CH), 6.90 (d, *J* 8.9, 2 × aryl =CH) and 7.07 (d, *J* 8.9, 2 × aryl =CH); δ_C 40.5, 55.3, 55.8, 56.0, 61.1, 83.5, 111.3, 113.0, 113.5, 120.3, 122.4, 126.4, 129.5, 131.5, 148.4, 149.0, 153.6, 158.6, 160.2 and 193.3 (Found: M^+, 398.1347. $C_{22}H_{22}O_7$ requires *M*, 398.1359).

6-*Bromo*-6-(3,4-*dimethoxybenzyl*)-3-*methoxy*-4-(4-*methoxyphenyl*)*pyran*-2,5-*dione* **14**.—A solution of bromine in acetic acid (1% v/v solution; 0.65 cm^3, 1 equiv.)[8] was added dropwise over 15 min to a stirred solution of compound **13b** (50 mg) in acetic acid (2 cm^3), under nitrogen. The mixture was stirred at room temperature for 2 h, diluted with water (10 cm^3) and extracted with ether (2 × 20 cm^3). The combined extracts were washed with water (6 × 20 cm^3), dried and evaporated to leave the *bromide* **14** (46 mg, 77%) as an orange oil, λ_{max}(EtOH)/nm 229 (ε 19 700), 254 (ε 13 000), 269 (ε 11 700) and 336 (ε 4 160); $\nu_{max}(CHCl_3)/cm^{-1}$ 2940m, 2840m, 1750s, 1685s, 1605s, 1495w, 1450m, 1335s, 1290s, 1140s, 1020m, 960w, 910w and 865w; δ_H 3.72 (d, *J* 14.2, 1 H), 3.82 (OMe), 3.84 (OMe), 3.85 (OMe), 3.86 (OMe), 3.95 (d, *J* 14.2, 1 H), 6.76 (d, *J* 8.1, 1 × aryl =CH), 6.84 (d, *J* 1.9, 1 × aryl =CH), 6.86 (dd, *J* 8.1 and 1.9, 1 × aryl =CH), 6.95 (d, *J* 8.9, 2 × aryl =CH) and 7.26 (d, *J* 8.9, 2 × aryl =CH); δ_C 46.1, 55.4, 55.9, 56.0, 61.5, 91.2, 111.1, 113.8, 114.3, 120.5, 123.9, 125.8, 127.8, 131.9, 148.6, 148.9, 150.4, 156.3, 160.6 and 185.9 (Found: M^+, 478.0463 and 476.0460. $C_{22}H_{21}BrO_7$ requires *M*, 478.0450 and 476.0470). The bromide was used without further purification.

6-(3,4-*Dimethoxybenzylidene*)-3-*methoxy*-4-(4-*methoxyphenyl*)*pyran*-2,5-*dione* **15**.—A solution of compound **14** (32 mg) in dry benzene (3 cm^3) was added dropwise to a stirred solution of 1,5-diazabicyclo[5.4.0]undec-5-ene (10 mm^3, 1 equiv.) in dry benzene (15 cm^3) under nitrogen. After 10 min a black precipitate formed. The mixture was poured onto hydrochloric acid (2 mol cm^{-3}; 10 cm^3) and extracted with ether (2 × 20 cm^3). The combined ether extracts were dried and evaporated to leave a residue which was purified by column chromatography to give the trimethylgrevillin (10.5 mg, 40%) as a solid which recrystallised from methanol as orange–yellow crystals, m.p. 175–176 °C (lit.,[10] 177–179 °C), λ_{max}(EtOH)/nm 230 (ε 14 000), 281 (ε 10 700), 336 (ε 12 000) and 410 (ε 5670); $\nu_{max}(CHCl_3)/cm^{-1}$ 2920m, 2830m, 1740s, 1680m, 1610s, 1590s, 1500w, 1460m, 1445m, 1425m, 1360s, 1340m, 1150s, 1100m, 1025m, 915s, 870w and 840w; δ_H 3.86 (OMe), 3.95 (2 × OMe), 3.97 (OMe), 6.93 (d, *J* 8.5, 1 × aryl =CH), 6.98 (d, *J* 8.9, 2 × aryl =CH), 7.04 (1 × =CH), 7.38 (d, *J* 8.9, 2 × aryl =CH), 7.50 (dd, *J* 2.0 and 8.5, 1 × aryl =CH) and 7.58 (d, *J* 2.0 H, 1 × aryl =CH); δ_C 55.3, 56.0, 61.3, 111.2, 113.6, 114.0, 120.3, 121.1, 125.1, 128.8, 131.8, 133.8, 143.1, 149.1, 150.9, 151.3, 155.4, 160.4 and 177.9 (Found: M^+, 369.1209. $C_{22}H_{20}O_7$ requires *M*, 369.1209).

3-*Hydroxy*-6-(3,4-*dihydroxybenzylidene*)-4-(4-*hydroxyphenyl*)-*pyran*-2,5-*dione* (*Grevillin B*) **3**.—A solution of boron tribromide in hexane (1 mol dm^{-3}; 177 mm^3, 7 equiv.) was added dropwise to a stirred solution of compound **15** (10 mg) in dry dichloromethane (10 cm^3) which was heated under reflux in a nitrogen atmosphere. The mixture was stirred and heated under reflux for a further 3.5 h, leading to a deep red precipitate. Concentrated hydrochloric acid[10] (2 cm^3) was added, and the mixture was then stirred vigorously for an additional 30 min. The mixture was poured onto water (15 cm^3) and then extracted with ethyl acetate (2 × 30 cm^3). The combined ethyl acetate extracts were washed successively with water (30 cm^3), saturated aqueous mannitol (30 cm^3) and water (30 cm^3) and then dried and evaporated to leave a solid residue. Purification by column chromatography on acetylated polyamide gave the 'free' grevillin (3.3 mg, 38%), which recrystallised from ethanol as red crystals, m.p. 258 °C (decomp.) [lit.,[1c] 275 °C (decomp.)/lit.,[10] 350 °C with 250 °C (decomp.)]; λ_{max}(EtOH)/nm 286 (ε 7250), 298sh (ε 6820) and 405 (ε 5650); ν_{max}(KBr)/cm^{-1} 3370br s, 3040s, 1725s, 1610m, 1580m, 1515m, 1450m, 1380m, 1300m, 1260s, 1230s, 1130m, 1045w, 1010w, 875w, 850w, 780w and 735w; δ_H([$^2H_6$]acetone) 6.88 (d, *J* 8.8, 2 × aryl =CH), 6.92 (1 × =CH), 6.92 (d, *J* 8.3, 1 × aryl =CH), 7.28 (dd, *J* 1.9 and 8.3, 1 × aryl =CH), 7.43 (d, *J* 8.8, 2 × aryl =CH) and 7.60 (d, *J* 1.9, 1 × aryl =CH) (Found: M^+, 340.0579. $C_{18}H_{12}O_7$ requires *M*, 340.0579). The spectral data were identical with those reported by Edwards[1c] and by Steglich[10] and their collaborators for the natural material.

3-*Phenyl*-2-*trimethylsilyloxypropanenitrile* **16a**.—Phenylacetaldehyde (13.6 g) was added dropwise to a stirred mixture of trimethylsilyl cyanide (15 cm^3, 1 equiv.) and zinc iodide (1 crystal) at 0 °C under a nitrogen atmosphere. The mixture was stirred for a further 15 min and then distilled to give the title compound (24.6 g, 99%),[17] as a colourless liquid, b.p. 90–94 °C at 0.5 mmHg, ν_{max}(liquid film)/cm^{-1} 2960br m, 1950w, 1720w, 1605w, 1500m, 1465m, 1365m, 1260s, 1115s, 940m, 880s, 860s, 765s and 705s; δ_H(no solvent) 0.00 (OTMS), 2.86 (d, *J* 6.3, CH_2), 4.42 (t, *J* 6.3, CH) and 7.15 (5 × aryl =CH).

3-*Hydroxy*-1,4-*diphenylbutan*-2-*one* **17a**.—A solution of compound **16a** (14 g) in dry ether (100 cm^3) was added dropwise to a solution of benzylmagnesium bromide (1.5 equiv.) in ether (400 cm^3) under reflux in an atmosphere of nitrogen. The mixture was heated under reflux for a further 3 h when a white precipitate formed. The mixture was allowed to cool to room temperature, and then poured onto ice cooled dilute hydrochloric acid (300 cm^3). The two-phase mixture was stirred vigorously at 25 °C overnight. The mixture was extracted with ether (2 × 200 cm^3), and the combined ether extracts were then dried and evaporated to leave a solid residue. Purification by column chromatography gave the title compound (13.75 g, 90%), which recrystallised from light petroleum as white prismatic crystals, m.p. 56–58 °C (lit.,[18] 59 °C), $\nu_{max}(CHCl_3)/cm^{-1}$ 3490m, 3020m, 2910m, 1705s, 1600w, 1490w, 1395m, 1325m, 1105m, 1050s and 910w; δ_H 2.80 (dd, *J* 7.3 and 14.1, CH), 3.10 (dd, *J* 4.8 and 14.1, CH), 3.31 (d, *J* 5.7, OH), 3.69 (CH_2), 4.40 (m, CH) and 7.00–7.40 (m, 10 × aryl =CH); δ_C 40.0, 45.4, 76.8, 126.7, 127.0, 128.4, 128.6, 129.3, 129.5, 133.3, 136.7 and 209.2 (Found: C, 80.15; H, 6.9%; M^+, 240.1160. Calc. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7%; *M*, 240.1151).

3-*Oxo*-1,4-*diphenylbutan*-2-*yl Ethyl Oxalate* **18a**.—A solution of compound **17a** (500 mg) and triethylamine (293 mm^3, 1 equiv.) in dry THF (15 cm^3) was added dropwise to a stirred solution of ethyl oxalyl chloride (235 mm^3, 1 equiv.) in dry THF (10 cm^3) under nitrogen, whereupon a white precipitate formed immediately. The mixture was stirred at 25 °C for 30 min, and then poured onto hydrochloric acid (2 mol dm^{-3}; 30 cm^3). The mixture was extracted with ether (2 × 30 cm^3), and the combined ether extracts were then dried and evaporated to leave an oily residue. Column chromatography of the latter gave the *oxalate* (480 mg, 68%), as a colourless oil, ν_{max}(liquid film)/cm^{-1} 3000br w, 1765s, 1745s, 1600w, 1495w, 1455w, 1310m, 1185s, 1010m, 920w, 865w, 750m and 750s; δ_H 1.28 (t, *J* 6.5, $CO_2CH_2CH_3$), 3.10 (dd, *J* 5.4 and 7.2, CH_2), 3.69 (CH_2), 4.25 (q, *J* 6.5, $CO_2CH_2CH_3$), 5.45 (dd, *J* 5.4 and 7.2, CH) and 7.00–7.45 (m, 10 × aryl =CH); δ_C 13.9, 36.9, 46.9, 63.4, 80.4, 127.3, 127.4, 128.7, 129.5, 129.7, 132.4, 135.0, 156.8, 156.9 and 202.9 (Found: M^+, 340.1315. $C_{20}H_{20}O_5$ requires *M*, 340.1310).

6-*Benzyl*-3-*hydroxy*-4-*phenylpyran*-2,5-*dione* **19a**.—A solution of compound **18a** (4 g) in dry DMF (30 cm^3) was added dropwise, over 15 min, to a stirred solution of 1,5-diazabicyclo[5.4.0]undec-5-ene (3.6 cm^3, 2 equiv.) in dry DMF (100 cm^3) at −15 °C under nitrogen. The resulting orange–red solution was stirred for a further 3 h and then poured onto hydrochloric acid (2 mol dm^{-3}; 100 cm^3). The mixture was extracted with ether (2 × 100 cm^3), and the combined ether extracts were then washed with water (3 × 75 cm^3), dried and evaporated to leave a cream solid. Recrystallisation of the latter

from heptane gave the *title compound* (3.14 g, 91%) as a white powder, m.p. 120–122 °C, λ_{max}(EtOH)/nm 235 (ε 11 540) and 307 (ε 8120); ν_{max}($CHCl_3$)/cm^{-1} 3400s, 3040br m, 1720s, 1665s, 1600w, 1490w, 1360s, 1280s, 1180s, 1075m, 1040m, 950w and 885w; δ_H 3.38 (d, *J* 4.7, CH_2), 5.31 (t, *J* 4.7, CH) and 7.10–7.45 (m, 10 × aryl =CH); δ_C 40.4, 84.7, 127.6, 128.0, 128.7, 129.0, 133.7, 149.0, 161.4 and 191.0 (Found: C, 73.3; H, 4.9%; M^+, 294.0877. $C_{18}H_{14}O_4$ requires: C, 73.5; H, 4.8%; *M*, 294.0892).

6-*Benzyl*-3-*methoxy*-4-*phenylpyran*-2,5-*dione* **20a**.—An ethereal solution of diazomethane was added to a solution of compound **19a** (500 mg) in ether (30 cm^3) at 0 °C, until the solution remained pale yellow. The mixture was stirred at 0 °C for 15 min, and then evaporated to dryness to leave an oily residue. Column chromatography gave the *title compound* (429 mg, 82%), as a colourless oil, λ_{max}(EtOH)/nm 228 (ε 6660), 248sh (ε 4150), 292 (ε 3130) and 302 (ε 3020); ν_{max}(liquid film)/cm^{-1} 3000br w, 1735s, 1675s, 1615m, 1600m, 1495w, 1445w, 1355m, 1330m, 1295m, 1210s, 1150s, 1080w, 1060w, 910w, 820w, 755s and 695s; δ_H 3.30 (d, *J* 4.5, CH_2), 3.44 (OMe), 5.18 (t, *J* 4.5, CH) and 6.90–7.40 (m, 10 × aryl =CH), δ_C 40.8, 61.3, 83.5, 127.6, 128.0, 128.5, 128.8, 129.1, 129.6, 130.0, 130.3, 134.0, 154.0, 158.2 and 192.6 (Found: M^+, 308.1048. $C_{19}H_{16}O_4$ requires *M*, 308.1049).

6-*Benzyl*-6-*bromo*-3-*methoxy*-4-*phenylpyran*-2,5-*dione* **21a**.—A solution of bromine in acetic acid (0.5% v/v solution; 12.9 cm^3, 1 equiv.) was added dropwise over 15 min to a stirred solution of compound **20a** (400 mg) in acetic acid (12 cm^3), under nitrogen. The mixture was stirred at room temperature for 3 h and then diluted with water (50 cm^3) and extracted with ether (2 × 50 cm^3). The combined ether extracts were washed with water (4 × 30 cm^3), dried and evaporated to leave the *bromide* (452 mg, 90%), as a light yellow oil, λ_{max}(EtOH)/nm 229 (ε 12 500), 291 (ε 6360) and 302 (ε 6070); ν_{max}(liquid film)/cm^{-1} 3000br m, 1750s, 1685s, 1610s, 1600s, 1495m, 1450s, 1430w, 1350s, 1310s, 1190s, 1130s, 1035w, 980w, 940m, 915m, 865m, 765s, 740s and 705s; δ_H 3.74 (d, *J* 14.1, CH), 3.81 (OMe), 4.00 (d, *J* 14.1, CH) and 7.15–7.50 (m, 10 × aryl =CH); δ_C 46.2, 61.6, 91.0, 127.8, 128.2, 128.5, 129.6, 130.2, 131.4, 133.3, 157.0 and 185.4 (3 carbons of low intensity not showing) (Found: M^+, 388.0167 and 386.0131. $C_{19}H_{15}BrO_4$ requires *M*, 388.0133 and 386.0154). The bromide was used without further purification.

6-*Benzylidene*-3-*methoxy*-4-*phenylpyran*-2,5-*dione* **22a**.—A solution of compound **21a** (420 mg) in dry benzene (10 cm^3) was added dropwise to a stirred solution of 1,5-diazabicyclo[5.4.0]-undec-5-ene (178 mm^3, 1.1 equiv.) in dry benzene (150 cm^3) under nitrogen. Initially a deep yellow solution was produced, which became cloudy and finally black within a few minutes. The mixture was poured onto hydrochloric acid (2 mol dm^{-3}; 50 cm^3) and then extracted with ether (2 × 100 cm^3). The combined ether extracts were dried and evaporated to leave an oily residue which was purified by column chromatography to give the methyl grevillin (75 mg, 22%), which recrystallised from heptane as yellow needles, m.p. 149–151 °C, λ_{max}(EtOH)/nm 232 (ε 9380), 246sh (ε 8500), 311sh (ε 5230) and 320 (ε 5300); ν_{max}($CHCl_3$)/cm^{-1} 1745s, 1670m, 1610s, 1460w, 1320s, 1180s, 1120m and 925w; δ_H 3.93 (OMe), 7.05 (1 × =CH), 7.22–7.52 (m, 8 × aryl =CH) and 7.78–8.00 (m, 2 × aryl =CH); δ_C 61.5, 120.0, 128.1, 129.0, 129.3, 130.2, 130.5, 131.9, 132.0, 144.0 and 178.0 (4 carbons of low intensity not showing) (Found: M^+, 306.0886. $C_{19}H_{14}O_4$ requires *M*, 306.0890).

6-*Benzylidene*-3-*hydroxy*-4-*phenylpyran*-2,5-*dione* **23**.—A solution of boron tribromide in hexane (1 mol dm^{-3}; 660 mm^3, 4 equiv.) was added dropwise to a stirred solution of compound **22a** (50 mg) in dry dichloromethane (12 cm^3) which was heated under reflux in a nitrogen atmosphere. The mixture was stirred and heated under reflux for a further 30 min after which the resulting orange solution was poured onto methanol (20 cm^3), and diluted with water (20 cm^3). The mixture was extracted with ether (2 × 30 cm^3), and the combined ether extracts were dried and evaporated to leave a solid residue. Column chromatography on acetylated polyamide gave the 'free' grevillin (44 mg, 92%), which recrystallised from ethanol as yellow plates, m.p. 233–235 °C (lit.,[19] 237–238 °C), λ_{max}(EtOH)/nm 201 (ε 16 400), 260 (ε 15 200) and 345 (ε 15 300); ν_{max}(KBr)/cm^{-1} 3300m, 1715s, 1590s, 1490w, 1445w, 1370s, 1210s, 995m, 760m, 735m and 695s; δ_H([$^2H_6$]-DMSO) 6.98 (1 × =CH), 7.30–7.60 (m, 8 × aryl =CH) and 7.85–8.00 (m, 2 × aryl =CH) (Found: C, 73.7; H, 4.2%; M^+, 292.0731. Calc. for $C_{18}H_{12}O_4$: C, 74.0; H, 4.1%; *M*, 292.0732).

3-(4-*Methoxyphenyl*)-2-*trimethylsilyloxypropanenitrile* **16b**.—4-Methoxyphenylacetaldehyde (2.75 g) was added dropwise onto a stirred mixture of trimethylsilyl cyanide (2.45 cm^3, 1 equiv.) and zinc iodide (1 crystal) at 0 °C under a nitrogen atmosphere. The mixture was stirred for a further 2 h and then distilled to give the title compound (2.71 g, 59%), as a colourless liquid, b.p. 70–75 °C at 0.5 mmHg, ν_{max}(liquid film)/cm^{-1} 2960m, 1610m, 1580w, 1510s, 1460w, 1440w, 1350w, 1300m, 1265s, 1180m, 1115s, 1035m, 935w, 885m, 850s and 760m; δ_H(no solvent) 0.00 (OTMS), 2.80 (d, *J* 7.0, CH_2), 3.52 (OMe), 4.37 (t, *J* 7.0, CH), 6.70 (d, *J* 8.5, 2 × aryl =CH) and 7.03 (d, *J* 8.5, 2 × aryl =CH).

3-*Hydroxy*-4-(4-*methoxyphenyl*)-1-*phenylbutan*-2-*one* **17b**.—A solution of compound **16b** (2.7 g) in dry ether (25 cm^3) was added dropwise to a refluxing ethereal solution (20 cm^3) of benzylmagnesium bromide (1.5 equiv.) under nitrogen. The mixture was stirred at ambient temperature overnight and then poured onto ice-cooled dilute hydrochloride acid (150 cm^3). The layers were separated and the organic phase was washed with brine (2 × 20 cm^3), dried and evaporated to leave a solid residue. Purification of the latter by column chromatography gave the title compound (1.9 g, 65%) which recrystallised from light petroleum as white crystals, m.p. 74–76 °C, ν_{max}($CHCl_3$)/cm^{-1} 3480m, 2910m, 1710s, 1610s, 1585m, 1440m, 1300s, 1275m, 1110m, 1030m and 910w; δ_H 2.80 (dd, *J* 7.1 and 14.2, 1 H), 3.10 (dd, *J* 4.9 and 14.2, 1 H), 3.22 (br, OH), 3.75 (CH_2), 3.76 (OMe), 4.45 (br, m, CH), 6.82 (d, *J* 8.8, 2 × aryl =CH) and 7.00–7.35 (m, 7 × aryl =CH); δ_C 39.4, 45.8, 55.4, 77.1, 114.2, 127.4, 128.9, 129.6, 130.4, 130.9, 133.2, 158.8 and 209.2 (Found: C, 75.6; H, 6.9%; M^+, 270.1241. $C_{17}H_{18}O_3$ requires C, 75.5; H, 6.7%; *M*, 270.1255).

Ethyl 1-(4-*Methoxyphenyl*)-4-*phenyl*-3-*oxobutan*-2-*yl Oxalate* **18b**.—A solution of compound **17b** (1.25 g) and triethylamine (0.62 cm^3, 1 equiv.) in dry THF (50 cm^3) was added dropwise to a stirred solution of ethyl oxalyl chloride (0.52 ml, 1 equiv.) in dry THF (50 cm^3), under nitrogen, whereupon a white precipitate formed immediately. The mixture was stirred at 25 °C for 30 min, and then poured onto hydrochloric acid (2 mol dm^{-3}; 50 cm^3). The mixture was extracted with ether (2 × 75 cm^3), and the combined ether extracts were then dried and evaporated to yield the *title compound* (1.68 g, 98%) as a light yellow oil, ν_{max}(liquid film)/cm^{-1} 2940br m, 1740br s, 1610w, 1510m, 1450m, 1300m, 1245s, 1180s, 1110w, 1040m, 825m, 730m and 695m; δ_H 1.38 (t, *J* 7.0 $CO_2CH_2CH_3$), 3.08 (d, *J* 6.3, CH_2), 3.70 (CH_2), 3.80 (OMe), 4.38 (q, *J* 7.0, $CO_2CH_2CH_3$), 5.37 (t, *J* 6.3, CH), 6.80 (d, *J* 9.0, 2 × aryl =CH) and 7.00–7.40 (m, 7 × aryl =CH); δ_C 13.9, 36.1, 47.0, 55.3, 63.4, 80.6, 114.1, 126.8, 127.3, 128.7, 129.7, 130.6, 132.4, 157.0, 158.9 and 203.1 (Found: M^+, 370.1416. $C_{21}H_{22}O_6$ requires *M*, 370.1414).

3-*Hydroxy*-6-(4-*methoxybenzyl*)-4-*phenylpyran*-2,5-*dione* **19b**.—A solution of compound **18b** (1.65 g) in dry DMF (50 cm^3) was added dropwise, over 15 min, to a stirred solution of 1,5-diazabicyclo[5.4.0]undec-5-ene (1.30 cm^3, 2 equiv.) in dry DMF (20 cm^3) at −15 °C, under nitrogen. The mixture was stirred for 2 h and then quenched by addition of dilute hydrochloric acid (50 cm^3). The mixture was extracted with ether (2 × 50 cm^3), and the combined ether extracts were then washed with water (3 × 50 cm^3), dried and evaporated to leave a crude residue. Column chromatography of the latter gave the *title compound* (1.06 g, 73%) as a pale yellow solid which recrystallised from heptane as yellow needles, m.p. 131–132 °C, λ_{max}(EtOH)/nm 226 (ε 20 600), 285 (ε 7350) and 305 (ε 7650); $\nu_{max}(CHCl_3)/cm^{-1}$ 3430m, 3000br w, 1730s, 1675s, 1615m, 1520w, 1365s, 1185w, 1120w, 955w, 890w and 845w; δ_H 3.34 (d, *J* 4.5, CH_2), 3.74 (OMe), 5.29 (t, *J* 4.5, CH), 6.78 (d, *J* 8.0, 2 × aryl =CH), 7.18–7.50 (m, 5 × aryl =CH) and 7.65 (d, *J* 8.0, 2 × aryl =CH); δ_C 39.7, 55.3, 85.0, 114.2, 122.2, 125.4, 127.7, 128.1, 129.2, 129.9, 131.2, 149.0, 159.2, 161.6 and 191.1 (Found: C, 70.4; H, 5.2%; M^+, 324.0989. $C_{19}H_{16}O_5$ requires C, 70.4; H, 5.0%; *M*, 324.0996).

3-*Methoxy*-6-(4-*methoxybenzyl*)-4-*phenylpyran*-2,5-*dione* **20b**.—An ethereal solution of diazomethane was added to a solution of compound **19b** (65 mg) in ether (3 cm^3) at 0 °C, until the solution remained pale yellow. The mixture was stirred at 0 °C for 30 min, and then evaporated to dryness to leave the *title compound* (66 mg, 97%) as a viscous yellow oil, λ_{max}(EtOH)/nm 225 (ε 18 000), 254 (ε 5800), 283 (ε 6540) and 294 (ε 6050); ν_{max}(liquid film)/cm^{-1} 3400br w, 2950br m, 1730s, 1675s, 1610s, 1600s, 1510s, 1445s, 1365s, 1300s, 1250s, 1205s, 1175s, 1145s, 1110m, 1060m, 1035s, 965w, 845m, 765m and 695m; δ_H 3.26 (d, *J* 4.0, CH_2), 3.52 (OMe), 3.73 (OMe), 5.18 (t, *J* 4.0, CH), 6.78 (d, *J* 8.0, 2 × aryl =CH), 7.04 (d, *J* 8.0, 2 × aryl =CH) and 6.93–7.40 (m, 5 × aryl =CH); δ_C 40.0, 55.3, 61.3, 83.7, 114.1, 125.9, 127.9, 128.0, 128.5, 129.1, 129.5, 130.0, 131.4, 159.1 and 192.8 (Found: M^+, 338.1136. $C_{20}H_{18}O_5$ requires *M*, 338.1155).

6-*Bromo*-3-*methoxy*-6-(4-*methoxybenzyl*)-4-*phenylpyran*-2,5-*dione* **21b**.—A solution of bromine in acetic acid (1% v/v solution; 0.81 cm^3, 1 equiv.) was added dropwise over 15 min to a stirred solution of compound **20b** (54 mg) in acetic acid (2 cm^3), under nitrogen. The mixture was stirred at ambient temperature for 2 h and then diluted with water (10 cm^3) and extracted with ether (2 × 20 cm^3). The combined ether extracts were washed with water (3 × 20 cm^3), dried and evaporated to give the title compound (36 mg, 54%) as a very unstable yellow oil, $\nu_{max}(CHCl_3)/cm^{-1}$ 2950br m, 1765s, 1695s, 1615s, 1605s, 1495m, 1450m, 1350s, 1310s, 1135s, 1035m 990w, 940w, 875w and 850w; δ_H 3.75 (OMe), 3.82 (OMe), 3.40–3.75 (m, CH_2), 6.80 (d, *J* 8.7, 2 × aryl =CH) and 7.10–7.55 (m, 7 × aryl =CH). The bromide was used without further purification.

3-*Methoxy*-6-(4-*methoxybenzylidene*)-4-*phenylpyran*-2,5-*dione* **22b**.—A solution of compound **21b** (98 mg) in dry benzene (10 cm^3) was added dropwise to a stirred solution of 1,5-diazabicyclo[5.4.0]undec-5-ene (35 mm^3, 1 equiv.) in dry benzene (60 cm^3) under nitrogen. After 45 min the mixture was poured onto dilute hydrochloric acid (25 cm^3) and extracted with ether (2 × 50 cm^3). The combined ether extracts were dried and evaporated to leave an oily residue which was purified by column chromatography to give the *title compound* (15 mg, 20%), which recrystallised from methanol as yellow needles, m.p. 162–163 °C, λ_{max}(EtOH)/nm 234 (ε 8610), 267 (ε 10 850) and 402 (ε 8080); $\nu_{max}(CHCl_3)$ 2940w, 1740s, 1665w, 1590s, 1510w, 1365m, 1315m, 1165s, 1110w, 1030w and 915w; δ_H 3.86 (OMe), 3.93 (OMe), 6.96 (d, *J* 8.9, 2 × aryl =CH), 7.04 (1 × =CH), 7.41 (5 × aryl =CH) and 7.90 (d, *J* 8.9, 2 × aryl=CH); δ_C 55.4; 61.4, 114.6, 120.3, 124.8, 128.1, 129.1, 129.2, 130.2, 133.7, 134.1, 142.9, 151.4, 155.4, 161.6 and 177.6 (Found: M^+, 336.1005. $C_{20}H_{16}O_5$ requires *M*, 336.0998).

3-*Hydroxy*-6-(4-*hydroxybenzylidene*)-4-*phenylpyran*-2,5-*dione* **24**.—A solution of boron tribromide in hexane (1 mol dm^{-3}; 255 mm^3, 5 equiv.) was added dropwise to a stirred solution of compound **22** (14 mg) in dry dichloromethane (10 cm^3) which was heated under reflux in a nitrogen atmosphere. The mixture was stirred and heated under reflux for a further 4 h after which concentrated hydrochloric acid[10] (3 cm^3) was added to it and the mixture was stirred vigorously for an additional 1 h. The mixture was poured onto water (15 cm^3) and extracted with ethyl acetate (2 × 30 cm^3). The combined ethyl acetate extracts were washed successively with water (30 cm^3), saturated aqueous mannitol (30 cm^3) and water (30 cm^3) and then dried and evaporated to leave a solid residue. Purification of this by column chromatography on acetylated polyamide gave the 'free' *grevillin* (5.4 mg, 42%), which recrystallised from ethanol as yellow–orange crystals, m.p. 240–248 °C (decomp.), λ_{max}(EtOH)/nm 264 (ε 13 400), 283 (ε 12 700) and 400 (ε 11 700); ν_{max}(KBr)/cm^{-1} 3400br s, 1640m, 1575s, 1515m, 1450w, 1380s, 1345m, 1245m, 1210s, 1175s, 1005w, 845w, 770w, 740w, and 700w; $\delta_H([^2H_6]$acetone) 6.98 (d, *J* 8.7, 2 × aryl =CH), 7.01 (1 × =CH), 7.30–7.48 (m, 3 × aryl =CH), 7.50–7.60 (m, 2 × aryl =CH) and 7.88 (d, *J* 8.7, 2 × aryl =CH); $\delta_C([^2H_6]$acetone) 116.8, 119.4, 124.9, 125.7, 128.4, 129.2, 131.3, 134.7, 144.1, 150.0, 158.3, 160.4 and 177.5 (Found: M^+, 308.0676. $C_{18}H_{12}O_5$ requires *M*, 308.0683).

3,6-*Dihydroxy*-2,5-*diphenyl*-1,4-*benzoquinone* (*Polyporic Acid*) **4a**.—A solution of compound **23** (50 mg) in dry ethanol (5 cm^3) was treated with sodium ethoxide (0.17 mol dm^{-3} solution; 1 cm^3, 1 equiv.).[11] A deep purple precipitate formed immediately and the mixture was stirred, at room temperature, under nitrogen for 30 min. The reaction was acidified with hydrochloric acid (2 mol dm^{-3}; 5 cm^3) and extracted with ether (2 × 20 cm^3). The ether extracts were dried and evaporated to give polyporic acid (45 mg, 90%), which recrystallised from acetone as dark brown needles, m.p. 300–301 °C (lit.,[13] 303–305 °C); λ_{max}(EtOH)/nm 262 (ε 21 300), 325 (ε 5330) and 475 (ε 254); ν_{max}(KBr)/cm^{-1} 3300s, 1610s, 1595sh s, 1325s, 1310s, 1250s, 1000s, 770m, 725m and 695m, $\delta_H([^2H_6]$-DMSO) 7.38 (10 × aryl =CH) (Found: M^+, 292.0721. $C_{18}H_{12}O_4$ requires *M*, 292.0732). The sample was identical with a specimen synthesised by the alternative route described by Shildneck and Adams.[13,20]

6-(4-*Benzyloxybenzylidene*)-3-*hydroxy*-4-*phenylpyran*-2,5-*dione* **25c**.—The grevillin which was prepared in 64% yield according to the method described by Steglich,[10] had m.p. 246–248 °C (lit.,[10] m.p. 247–249 °C), λ_{max}(EtOH)/nm 238sh (ε 11 350), 256 (ε 12 560), 285sh (ε 9150), 362sh (ε 13 110) and 383 (ε 14 350); ν_{max}(KBr)/cm^{-1} 3300m, 1720s, 1640w, 1580s, 1500m, 1375s, 1250s, 1200s, 1170s, 995m, 830m, 730m and 695m; $\delta_H([^2H_6]$-DMSO) 5.21 (CH_2), 6.99 (1 × =CH), 7.17 (d, *J* 8.8, 2 × aryl =CH), 7.30–7.60 (m, 10 × aryl =CH) and 7.93 (d, *J* 8.8, 2 × aryl =CH) (Found: C, 75.5; H, 4.6%; M^+, 398.1148. Calc. for $C_{25}H_{18}O_5$: C, 75.4; H, 4.6%; *M*, 398.1149).

3,6-*Dihydroxy*-2-(4-*methoxyphenyl*)-5-*phenyl*-1,4-*benzoquinone* **4b**.—A suspension of compound **25b** (50 mg) in dry methanol (3 cm^3) was treated with sodium methoxide (2.6 mol dm^{-3} solution; 1.6 cm^3, 2.6 equiv.), whereupon a deep purple precipitate formed almost immediately. The mixture was stirred for 30 min under nitrogen and then acidified with hydrochloric acid (2 mol dm^{-3}, 5 cm^3). The green precipitate which formed was collected by vacuum filtration to give the

terphenylquinone (41 mg, 82%), which recrystallised from ethanol as greenish black microcrystalline square plates, m.p. 272–274 °C (lit.,[11] m.p. 280 °C), λ_{max}(EtOH)/nm 267 (ε 22 520), 350 (ε 3513), 497 (ε 500); ν_{max}(KBr)/cm^{-1} 3320s, 1615s, 1515m, 1450w, 1330s, 1315s, 1260s, 1190m, 1040m, 1005s, 845m, 810m, 775m, 735m and 705m; δ_H([$^2H_6$]-DMSO) 3.79 (OMe), 6.97 (d, *J* 8.9, 2 × aryl =CH), 7.35 (d, *J* 8.9, 2 × aryl =CH) and 7.30–7.40 (m, 5 × aryl =CH) (Found: M$^+$, 322.0844. $C_{19}H_{14}O_5$ requires *M*, 322.0840).

3-*Methoxy*-6-(4-*hydroxybenzylidene*)-4-*phenylpyran*-2,5-*dione* **25b**.—A solution of boron tribromide in hexane (1 mol dm^{-3}; 67 mm^3, 5 equiv.) was added dropwise to a stirred solution of compound **22b** (4.5 mg) in dry dichloromethane (5 cm^3), which was heated under reflux in a nitrogen atmosphere. The mixture was stirred and heated under reflux for a further 30 min after which concentrated hydrochloric acid (1 cm^3) was added, and the mixture was stirred vigorously for an additional 30 min. The mixture was poured onto water (10 cm^3) and then extracted with ethyl acetate (2 × 20 cm^3). The combined ethyl acetate extracts were washed successively with water (20 cm^3), saturated aqueous mannitol (20 cm^3) and water (20 cm^3) and then dried and evaporated to leave a solid residue. Purification of the latter by column chromatography on acetylated polyamide gave the 'free' *grevillin* (2 mg, 46%), which recrystallised from methanol as orange crystals, m.p. 216–218 °C, λ_{max}(EtOH)/nm 244sh (ε 13 500), 260 (ε 16 800), 280sh (ε 13 600) and 387 (ε 13 900); ν_{max}(KBr)/cm^{-1} 3320m, 1725s, 1655m, 1590s, 1515m, 1430w, 1380s, 1310s, 1265s, 1210s, 1185s, 1100w, 1035m, 1015w, 840m, 760m and 705m; δ_H([$^2H_6$]-acetone) 3.89 (OMe), 7.03 (1 × =CH), 7.07 (d, *J* 8.9, 2 × aryl =CH), 7.30–7.60 (m, 5 × aryl =CH) and 7.94 (d, *J* 8.9, 2 × aryl =CH); δ_C([$^2H_6$]-acetone) 55.8, 115.3, 119.0, 125.6, 125.8, 128.4, 129.2, 130.9, 131.3, 134.3, 144.3, 150.1, 158.2, 162.2 and 177.5 (Found: M$^+$, 322.0846. $C_{19}H_{14}O_5$ requires *M* 322.0841).

2-(4-*Benzyloxyphenyl*)-3,6-*dihydroxy*-5-*phenyl*-1,4-*benzoquinone* **4c**.—A solution of compound **25c** (97 mg) in dry ethanol (3 cm^3) was treated with sodium ethoxide (2.6 mol dm^{-3} solution; 2 ml, 2 equiv.). A deep purple precipitate formed immediately and the mixture was stirred, at room temperature, under nitrogen for 30 min. The reaction was acidified with hydrochloric acid (2 mol dm^{-3}; 5 cm^3) to give a green precipitate, which was collected by vacuum filtration and dried to give the terphenylquinone (89 mg, 92%), which recrystallised from ethanol as black plates, m.p. 268–270 °C (lit.,[11] m.p. 278 °C), λ_{max}(EtOH)/nm 270 (ε 49 000), 349 (ε 3710) and 494 (ε 340); ν_{max}(KBr)/cm^{-1} 3300s, 1605br s, 1510m, 1320s, 1250s, 1180m, 995s, 835w, 800w, 765w, 720w and 695w; δ_H([$^2H_6$]-DMSO) 5.15 (CH_2), 7.04 (d, *J* 9.0, 2 × aryl =CH) and 7.25–7.55 (m, 12 × aryl =CH) (Found: C, 75.7; H, 4.8%; M$^+$, 98.1145. Calc. for $C_{25}H_{18}O_5$: C, 75.4; H, 4.6%; *M*, 398.1149).

5-*Hydroxy*-3-(4-*hydroxyphenyl*)-4,7-*diphenylbenzofuran*-2,6-*dione* (*Xylerythrin*) **29a**.—A solution of polyporic acid **4a** (50 mg) and 4-hydroxyphenylacetic acid (26 mg) in acetic anhydride (1 cm^3), containing an excess of sodium acetate (5 equiv.) was heated under reflux for 3 h. The acetic anhydride was decomposed by the addition of water (1 cm^3) after which a mixture of 48% hydrogen bromide (1 cm^3) and acetic acid (1 cm^3) was added. The mixture was heated under reflux for 0.5 h and then cooled to room temperature and diluted with water (15 cm^3). The mixture was extracted with chloroform (3 × 15 cm^3), and the combined chloroform extracts were then dried and evaporated to leave a solid residue. Purification by column chromatography gave xylerythrin (27 mg, 39%), as black crystals with a green lustre, m.p. 263–267 °C ($CHCl_3$) (lit.,[14] m.p. 265–268 °C, lit.,[21] m.p. 253–255 °C), λ_{max}(EtOH)/nm 254 (ε 26 600), 359 (ε 9300) and 465 (ε 14 050); ν_{max}(KBr)/cm^{-1} 3600–3100br m, 1770m, 1740w, 1615m, 1600s, 1500w, 1400m, 1325m, 1270m, 1150m, 1015m, 835w, 750m and 695m; δ_H([$^2H_6$]acetone) 6.49 (d, *J* 8.9, 2 × aryl =CH), 6.96 (d, *J* 8.9, 2 × aryl =CH), 7.05–7.15 (m, 3 × aryl =CH), 7.15–7.30 (m, 2 × aryl =CH), 7.40–7.55 (m, 3 × aryl =CH) and 7.60–7.70 (m, 2 × aryl =CH); δ_C([$^2H_6$]acetone) 115.0, 115.3, 121.0, 128.3, 128.4, 128.8, 129.3, 130.6, 130.8, 131.2, 131.5, 132.6, 132.8, 133.7, 137.8, 148.5, 158.5, 159.6, 168.2 and 181.4 (Found: M$^+$, 408.1006. $C_{26}H_{16}O_5$ requires *M*, 408.0993). Identical spectral data were recorded for an authentic sample of natural xylerythrin.[14]

5-*Hydroxy*-3,4-*bis*(-*hydroxyphenyl*)-7-*phenylbenzofuran*-2,6-*dione* (*Peniophorin*) **29b** *and* 5-*Hydroxy*-3,7-*bis*(4-*hydroxyphenyl*)-4-*phenylbenzofuran*-2,6-*dione* (*Isopeniophorin*) **29c**.—A solution of compound **4c** (40 mg) and 4-hydroxyphenylacetic acid (1 equiv.) in acetic anhydride (1 cm^3), containing an excess of sodium acetate (5.25 equiv.) was heated under reflux for 3 h. The acetic acid was decomposed by the addition of water (1 cm^3), and then a mixture of 48% hydrogen bromide (1 cm^3) and acetic acid (1 cm^3). The mixture was heated under reflux for 0.5 h and then cooled to room temperature and diluted with water (15 cm^3). The mixture was extracted with chloroform (2 × 15 cm^3), and the combined organic extracts were then dried, and evaporated to give a solid residue containing both isopeniophorin and peniophorin. The isomers were separated by column chromatography to give: (i) isopeniophorin (eluted first) (9 mg, 22%), m.p. 298–307 °C (decomp.), ($CHCl_3$–AcOEt); λ_{max}(EtOH)/nm 263 (ε 20 000), 302sh (ε 8600), 400sh (ε 4400) and 470 (ε 9500); ν_{max}(KBr)/cm^{-1} 3470s, 3330s, 2930w, 1765s, 1600s, 1595s, 1505w, 1405m, 1330s, 1280m, 1225m, 1180m, 1150m, 1030m, 845w and 700w; δ_H([$^2H_6$]acetone) 6.50 (d, *J* 8.6, 2 × aryl =CH), 6.90–7.00 (m, 4 × aryl =CH), 7.05–7.15 (m, 3 × aryl =CH), 7.17–7.25 (m, 2 × aryl =CH) and 7.53 (d, *J* 8.7, 2 × aryl =CH); δ_C([$^2H_6$]acetone) 115.2, 115.7, 121.1, 121.5, 128.2, 128.3, 128.8, 129.2, 130.8, 131.6, 132.5, 132.7, 133.0, 138.1, 148.5, 157.8, 158.5, 168.5 and 181.8 (Found: M$^+$, 424.0959. $C_{26}H_{16}O_6$ requires *M*, 424.0942) and (ii) peniophorin (eluted second) (4.5 mg, 11%), m.p. 287–293 °C (decomp.) ($CHCl_3$) [lit.,[22] m.p. 300–305 °C (decomp.)]; λ_{max}(EtOH)/nm 268 (ε 23 400), 302sh (ε 7980), 389sh (ε 6500), 410sh (ε 7100) and 468 (ε 8780); ν_{max}(KBr)/cm^{-1} 3550m, 3300m, 1775s, 1695m, 1625s, 1600s, 1400w, 1330m, 1100w, 1010w, 980w, 890w and 830w; δ_H([$^2H_6$]acetone) 6.56 (d, *J* 8.8, 2 × aryl =CH), 6.58 (d, *J* 8.7, 2 × aryl =CH), 7.01 (d, *J* 8.8, 2 × aryl =CH), 7.06 (d, *J* 8.7, 2 × aryl =CH), 7.45–7.55 (m, 3 × aryl =CH) and 7.60–7.68 (m, 2 × aryl =CH); δ_C([$^2H_6$]acetone) 115.2, 121.1, 123.4, 128.3, 128.8, 129.3, 130.0, 130.4, 130.7, 131.1, 131.5, 132.0, 132.7, 133.0, 138.1, 148.1, 157.9, 159.6 and 168.3 (Found: M$^+$, 424.0958. $C_{26}H_{16}O_6$ requires *M*, 424.0942). Identical spectral data were recorded for an authentic sample of natural peniophorin.[22]

3-(4-*Aminophenyl*)-5-*hydroxy*-4,7-*diphenylbenzofuran*-2,6-*dione* **29d**.—A solution of polyporic acid (50 mg) and 4-aminophenylacetic acid (1.2 equiv.) in acetic anhydride (1 cm^3) containing an excess of sodium acetate (5 equiv.) was heated under reflux for 3 h. The acetic anhydride was decomposed by addition of water (1 cm^3), and then a mixture of 48% hydrobromic acid (1 cm^3) and acetic acid (1 cm^3) was added. The mixture was heated under reflux for 0.5 h and then cooled to room temperature and diluted with water (15 cm^3). The mixture was extracted with chloroform (2 × 15 cm^3), and the combined organic extracts were then dried and evaporated to leave the aminoxylerythrin (6 mg, 10%), which recrystallised from chloroform as blue crystals, m.p. 233–240 °C (decomp.); λ_{max}(EtOH)/nm 252sh (ε 18 300), 258 (ε 18 500), 359 (ε 6410) and 561 (ε 6940); ν_{max}(KBr)/cm^{-1} 3400br s, 1780m, 1625s, 1605s,

1515m, 1450w, 1415m, 1340m, 1315m, 1195w, 1165m, 1030m, 900w, 840w, 815w, 765w, 705m and 625w; δ_H([$^2H_6$]acetone) 6.30 (d, *J* 8.8, 2 × aryl =CH), 6.90 (d, *J* 8.8, 2 × aryl =CH), 7.15–7.25 (m, 3 × aryl =CH), 7.25–7.35 (m, 2 × aryl =CH), 7.40–7.55 (m, 3 × aryl =CH) and 7.60–7.70 (m, 2 × aryl =CH); δ_C([$^2H_6$]-acetone) 113.6, 117.8, 119.5, 128.3, 128.5, 128.8, 129.2, 130.8, 131.5, 131.8, 133.2, 134.8, 138.0, 148.2, 151.4, 168.4 and 181.3 (2 carbons low intensity not showing) (Found: M^+, 407.1149. $C_{26}H_{17}NO_4$ requires *M*, 407.1155).

5-*Hydroxy*-3,4,7-*triphenylbenzofuran*-2,6-*dione*(*Deoxyxylerythrin*) **29e**—A solution of polyporic acid (50 mg) and phenylacetic acid (1 equiv.) in acetic anhydride (1 cm^3) containing an excess of sodium acetate (5 equiv.) was heated under reflux for 3 h. The acetic anhydride was decomposed by addition of water (1 cm^3), and then a mixture of 48% hydrobromic acid (1 cm^3) and acetic acid (1 cm^3) was added. The mixture was heated under reflux for 0.5 h, cooled to room temperature and then diluted with water (15 cm^3). The mixture was extracted with chloroform (2 × 15 cm^3) and the combined organic extracts were then dried and evaporated to leave a solid residue.

Purification by column chromatography gave the deoxyxylerythrin (13 mg, 20%) as red crystals, m.p. 215–220 °C (decomp.) ($CHCl_3$); λ_{max}(EtOH)/nm 251 (ε 20 700), 282sh, 391sh, 396 (ε 12 700) and 476 (ε 1110); ν_{max}(KBr)/cm^{-1} 3600–3200br s, 1775s, 1630s, 1610s, 1445w, 1410w, 1335m, 1310m, 1200w, 1150w, 1025w, 935w, 785w, 755m and 700m; δ_H([$^2H_6$]-acetone) 7.00–7.10 (m, 5 × aryl =CH), 7.10–7.40 (m, 5 × aryl =CH), 7.45–7.60 (m, 3 × aryl =CH) and 7.60–7.70 (m, 2 × aryl =CH); δ_C([$^2H_6$]-acetone) 114.9, 115.4, 126.2, 128.1, 128.3, 128.4, 128.9, 129.4, 129.6, 130.7, 130.8, 131.5, 140.4, 148.8, 158.3, 167.8 and 181.6 (Found: M^+, 392.1031. $C_{26}H_{16}O_4$ requires *M*, 392.1044).

3,6-*Diphenylfuro*[3,2-b]*furan*-2,5-*dione* (*Pulvinic Anhydride*) **30a**.—A solution of polyporic acid (50 mg) in dimethyl sulphoxide (2 cm^3) and acetic anhydride (1 cm^3) was warmed to 100 °C in a nitrogen atmosphere for 15 min.[15] The cooled mixture was diluted with water (10 cm^3), and then extracted with chloroform (2 × 30 cm^3). The combined chloroform extracts were washed successively with brine (2 × 30 cm^3) and saturated aqueous sodium hydrogencarbonate (20 cm^3) and then dried and evaporated to leave the dilactone (44 mg, 89%), which recrystallised from chloroform as yellow microcrystalline plates, m.p. 226–228 °C (lit.,[15] m.p. 221–222 °C); λ_{max}(EtOH)/nm 233 (ε 9600), 288sh (ε 6170) and 373 (ε 10 200); ν_{max}(KBr)/cm^{-1} 1820s, 1795sh s, 1660s, 1495m, 1450m, 1365s, 1340s, 1320m, 1195w, 1165m, 1055m, 1005w, 920w, 875s, 800s, 780s, 730m, 690s, and 660m; δ_H([$^2H_6$]-DMSO) 7.10–7.40 (m, 8 × aryl =CH) and 8.12 (dd, *J* 8.4 and 1.2, 2 × aryl =CH); δ_C([$^2H_6$]-DMSO) 95.0, 117.5, 121.1, 125.2, 126.8, 127.1, 127.8, 130.0, 132.3, 135.8, 152.3, 166.9, 168.3 and 170.6 (Found: C, 74.1; H, 3.6%; M^+, 290.0564. Calc. for $C_{18}H_{10}O_4$: C, 74.5; H, 3.5%; *M*, 290.0579).

(E)-4-*Hydroxy*-5-(α-*methoxycarbonylbenzylidene*)-3-*phenylfuran*-2-(5H)-*one* (*Vulpinic Acid*) **31a**.—Aqueous sodium hydroxide (18 mol dm^{-3}; 0.9 cm^3) was added to a suspension of pulvinic anhydride (1.7 g) in methanol (25 cm^3), and after 5 min the resulting clear solution was diluted with water (25 cm^3) and acidified with concentrated hydrochloric acid. The precipitate was filtered off, and then placed under high vacuum for several hours to leave vulpinic acid (1.79 g, 95%) as a solid which recrystallised from methanol as yellow square plates, m.p. 150–151 °C (lit.,[23] m.p. 148 °C); λ_{max}(EtOH)/nm 234 (ε 11 986), 276 (ε 10 318), 366 (ε 11 106); ν_{max}($CHCl_3$)/cm^{-1} 3000br w, 2640br w, 1780s, 1680m, 1615s, 1605s, 1435m, 1315s, 1280s, 1065m, 965m and 905m; δ_H 3.86 (CO_2Me), 7.20–7.60 (m, 8 × aryl =CH), 8.10–8.30 (m, 2 × aryl =CH) and 13.87 (OH); δ_C 54.5, 105.2, 115.8, 127.9, 128.1, 128.3, 128.4, 128.6, 128.9, 129.9, 131.9, 154.9, 160.2, 165.9 and 171.7 (Found: C, 70.8; H, 4.3%; M^+, 322.0832. Calc. for $C_{19}H_{14}O_5$: C, 70.8; H, 4.4%; *M*, 322.0839).

(E)-4-*Methoxy*-5(-α-*methoxycarbonylbenzylidene*)-3-*phenylfuran*-2(5H)-*one* (*Permethylated Pulvinic Acid*) **32a**.—An ethereal solution of diazomethane was added to a suspension of vulpinic acid (1.7 g) in ether (85 cm^3) at 0 °C, until the solution remained pale yellow. The solution was stirred at 0 °C for 3 h after which it was evaporated to leave permethylated pulvinic acid (1.52 g, 86%), as a solid which recrystallised from methanol as cream rods, m.p. 140–141 °C (lit.,[24] m.p. 142–143 °C), λ_{max}($CHCl_3$)/cm^{-1} 224 (ε 7940), 233 (ε 11 613) and 331 (ε 22 129); ν_{max}($CHCl_3$)/cm^{-1} 3000br w, 1770s, 1730s, 1630s, 1600m, 1490w, 1440w, 1370m, 1325m, 1300m, 1160m, 1130w, 1030w, 980m, 930m; δ_H 3.74 (CO_2Me), 3.85 (OMe), 7.25–7.50 (m, 8 × aryl =CH) and 7.59–7.75 (m, 2 × aryl =CH); δ_C 52.8, 61.3, 108.2, 116.4, 128.4, 128.5, 128.8, 129.0, 129.1, 129.4, 130.0, 131.0, 141.4, 162.6, 167.1 and 167.8 (Found: C, 71.3; H, 4.8%; M^+, 336.1001. Calc. for $C_{20}H_{16}O_5$: C, 71.4; H, 4.8%; *M*, 336.0996).

(E)-5-(α-*Carboxybenzylidene*)-4-*hydroxy*-3-*phenylfuran*-2(5H)-*one* (*Pulvinic Acid*) **5a**.—A deuteriochloroform solution of permethylated pulvinic acid (32 mg) was treated with iodotrimethylsilane (68 cm^3, 5 equiv.)[5] in a ^1H NMR tube, sealed under nitrogen and warmed at 55 °C. The reaction was monitored by ^1H NMR spectroscopy, following the disappearance of the methyl group signals, with concomitant formation of methyl iodide. After 3 d the persilylated pulvinic acid was hydrolysed with methanol (6 cm^3), and the mixture was then evaporated to give the crude product. Column chromatography gave the pulvinic acid (18 mg, 61%), which recrystallised from chloroform as orange elongated plates, m.p. 202–208 °C (lit.,[25] m.p. 202–207 °C, lit.,[26] m.p. 216–217 °C), λ_{max}(EtOH)/nm 241 (ε 13 127), 253 (ε 12 596) and 362 (ε 12 152); ν_{max}(KBr)/cm^{-1} 3450m, 3000br w, 2500br w, 1750s, 1680m, 1620s, 1595s, 1500w, 1450m, 1375m, 1305w, 1270w, 1230w, 1170w, 1080w, 1065w, 970m, 920w, 790m, 730m and 700m; δ_H([$^2H_6$]-acetone) 7.30–7.55 (m, 8 × aryl =CH) and 8.05–8.20 (m, 2 × aryl =CH); δ_C([$^2H_6$]-acetone) 104.3, 117.5, 128.3, 128.7, 128.9, 129.1, 129.2, 130.3, 131.0, 134.2, 155.6, 162.2, 166.6 and 174.0 (Found: M^+, 308.0677. $C_{18}H_{12}O_5$ requires *M*, 308.0685).

6-(4-*Methoxyphenyl*)-3-*phenylfuro*[3,2-b]*furan*-2,5-*dione* (4-*Methoxypulvinic Acid Dilactone*) **30b**.—A solution of compound **4b** (26 mg) in dimethyl sulphoxide (0.4 cm^3) and acetic anhydride (0.2 cm^3) was warmed to 100 °C in a nitrogen atmosphere for 15 min. The mixture was cooled in an ice-bath and then the orange–yellow precipitate was filtered off. The solid was washed with water (5 cm^3) and then dried *in vacuo* to leave the dilactone (18 mg, 62%), which recrystallised from benzene as orange microcrystalline plates, m.p. 201–203 °C (lit.,[27] m.p. 200–201 °C), λ_{max}($CHCl_3$)/nm 243 (ε 18 416) and 410 (ε 22 865); ν_{max}($CHCl_3$)/cm^{-1} 3000br w, 1825s, 1790sh s, 1670s, 1610s, 1500w, 1365m, 1345m, 1320m, 1305m, 1165m, 1030w, 875s, 840m and 660m; δ_H 3.87 (OMe), 7.00 (d, *J* 9.0, 2 × aryl =CH), 7.40–7.55 (m, 3 × aryl =CH) and 7.90–8.05 (m, 4 × aryl =CH); δ_C 55.4, 100.9, 101.6, 114.7, 119.0, 126.6, 128.0, 129.1, 129.9, 155.1, 157.3, 161.0, 166.0 and 166.1 (Found: C, 71.3; H, 3.6%; M^+, 320.0687. Calc. for $C_{19}H_{12}O_5$: C, 71.25; H, 3.8%; *M*, 320.0683).

(E)-4-*Hydroxy*-5-(α-*methoxycarbonylbenzylidene*)-3-(4-*methoxyphenyl*)*furan*-2-(5H)-*one* (*Pinastric Acid*) **31c** *and* (E)-4-*Hydroxy*-5-(α-*methoxycarbonyl*-4-*methoxybenzylidene*)-3-*phenylfuran*-2-(5H)-*one* (*Isopinastric Acid*) **31b**.—Aqueous sodium hydroxide (18 mol dm^{-3} solution; 0.92 cm^3, 2.8 equiv.) was

added to a suspension of 4-methoxypulvinic dilactone (1.9 g) in methanol (25 cm^3), and after 5 min the resulting clear solution was diluted with water (25 cm^3) and acidified with concentrated hydrochloric acid. The resulting precipitate was filtered off to give a 4:1 mixture (1.98 g, 95%) of the two pulvinates **31b** and **31c**. The mixture of isomers was boiled in methanol, and the insoluble pinastric acid **31c** was filtered off. It recrystallised from benzene as rectangular plates, m.p. 207–209 °C (lit.,[28] m.p. 202–204 °C), λ_{max}(EtOH)/nm 208, 290 and 400; ν_{max}($CHCl_3$)/cm^{-1} 3000w, 2620w, 1775m, 1675m, 1600s, 1435w, 1110s, 1030w and 965m; δ_H 3.84 (OMe), 3.87 (CO_2Me), 6.96 (d, *J* 9.2, 2 × aryl =CH), 7.23–7.45 (m, 5 × aryl =CH), 8.12 (d, *J* 9.2, 2 × aryl =CH) and 13.50 (OH) (Found: C, 68.6; H, 4.5%; M^+, 352.0931. Calc. for $C_{20}H_{16}O_6$: C, 68.2; H, 4.6%; *M*, 352.0942). The filtrate was evaporated to dryness and the residue was crystallised from methanol to give isopinastric acid **31b**, as microneedles, m.p. 122–124 °C (lit.,[28] m.p. 127–129 °C), λ_{max}(EtOH)/nm 210, 229, 273 and 375; ν_{max}($CHCl_3$)/cm^{-1} 2960w, 2620w, 1770s, 1680s, 1430m, 1320s, 1050m, 965s and 910m; δ_H 3.85 (OMe), 3.89 (CO_2Me), 6.93 (d, *J* 9.2, 2 × aryl =CH), 7.10–7.45 (m, 5 × aryl =CH), 8.00–8.20 (m, 2 × aryl =CH) and 13.67 (OH) (Found: C, 68.3; H, 4.4%; M^+, 352.0947. Calc. for $C_{20}H_{16}O_6$: C, 68.2; H, 4.6%; *M*, 352.0942).

(E)-4-*Methoxy*-5-(α-*methoxycarbonyl*-4-*methoxybenzylidene*)-3-*phenylfuran*-2(5H)-*one* (*O-Methylisopinastric Acid*) **32c**.—An ethereal solution of diazomethane was added to a suspension of isopinastric acid (400 mg) in ether (40 cm^3) at 0 °C, until the ether solution remained pale yellow. The solution was stirred at 0 °C for 3 h and the solvent was then removed to leave *O*-methylisopinastric acid (426 mg, 95%) which recrystallised from methanol as yellow needles, m.p. 171–173 °C (lit.[28] m.p. 172–175 °C), λ_{max}($CHCl_3$)/nm 358 (ε 24 600); ν_{max}($CHCl_3$)/cm^{-1} 2940w, 1760s, 1725s, 1630s, 1600s, 1370m, 1290m, 1160m, 985m and 940m; δ_H 3.76 (OMe), 3.84 (OMe), 3.89 (CO_2Me), 6.93 (d, *J* 8.9, 2 × aryl =CH), 7.40–7.70 (m, 5 × aryl =CH) and 7.65 (d, *J* 8.9, 2 × aryl =CH) (Found: C, 69.1; H, 5.0%; M^+, 366.1141. Calc. for $C_{21}H_{18}O_6$: C, 68.8; H, 4.95%; *M*, 366.1098).

(E)-4-*Methoxy*-5-(α-*methoxycarbonylbenzylidene*)-3-(4-*methoxyphenyl*)*furan*-2(5H)-*one* [*O-Methylpinastric Acid*] **32b**.—An ethereal solution of diazomethane was added to a suspension of pinastric acid (100 mg) in ether (10 cm^3) at 0 °C, until the ether solution remained pale yellow. The solution was stirred at 0 °C for 3 h and then evaporated to leave *O*-methylpinastric acid (106 mg, 95%), which recrystallised from benzene as pale yellow microcrystals, m.p. 140–142 °C (lit.,[5] m.p. 140–141 °C), λ_{max}($CHCl_3$)/nm 342 (ε 19 400); ν_{max}($CHCl_3$)/cm^{-1} 2940w, 1770s, 1730s, 1635m, 1605s, 1300m, 1160m and 930m; δ_H 3.79 (OMe), 3.84 (OMe), 3.90 (CO_2Me), 6.96 (d, *J* 9.2, 2 × aryl =CH), 7.30–7.45 (m, 3 × aryl =CH), 7.50 (d, *J* 9.2, 2 × aryl =CH) and 7.60–7.80 (m, 2 × aryl =CH) (Found: C, 68.7; H, 5.0%; M^+, 366.1135. Calc. for $C_{21}H_{18}O_6$: C, 68.8; H, 4.95%; *M*, 366.1098).

(E)-5-(α-*Carboxy*-4-*hydroxybenzylidene*)-4-*hydroxy*-3-*phenylfuran*-2(5H)-*one* (*4′-Hydroxypulvinic Acid*) **5d**.—A solution of *O*-methylisopinastric acid (74 mg) in deuteriochloroform (1 cm^3) was treated with iodotrimethylsilane (173 mm^3, 6 equiv.) in a ^1H NMR tube, sealed under nitrogen and warmed to 55 °C. The reaction was monitored by ^1H NMR spectroscopy and after 3 d the resulting persilylated pulvinic acid was hydrolysed with methanol (6 cm^3). The solvent was evaporated to leave a solid residue which was purified by column chromatography to give 4′-hydroxypulvinic acid (22 mg, 34%), m.p. 95–99 °C (resolidify 105 °C, remelt 266–289 °C), λ_{max}(EtOH)/nm 244 (ε 12 300), 263 (ε 14 500) and 367 (ε 9500); λ_{max}(EtOH + 1 drop NaOH)/nm 257 (ε 13 100), 267 (ε 12 600) and 383 (ε 20 400); ν_{max}(KBr)/cm^{-1} 3400br m, 3000br w, 2550br w, 1745m, 1675w, 1605s, 1595s, 1510w, 1445m, 1370m, 1265m, 1060m, 965m, 920w, 785m and 690m; δ_H([$^2H_6$]acetone) 6.90 (d, *J* 8.9, 2 × aryl =CH), 7.29 (d, *J* 8.9, 2 × aryl =CH), 7.20–7.45 (m, 3 × aryl =CH) and 8.06–8.17 (m, 2 × aryl =CH) (Found: M^+, 324.0562. $C_{18}H_{12}O_6$ requires *M*, 324.0630). An accurate combustion analysis could not be obtained for this compound.

(E)-(5-(α-*Carboxybenzylidene*)-4-*hydroxy*-3-(4-*hydroxyphenyl*)*furan*-2(5H)-*one* (4-*Hydroxypulvinic Acid*) **5e**.—A solution of pinastric acid (29 mg) in deuteriochloroform (1 cm^3) was treated with iodotrimethylsilane (68 cm^3, 6 equiv.) in a ^1H NMR tube, sealed under nitrogen and warmed to 55 °C. The reaction was conveniently monitored by ^1H NMR spectroscopy and after 3 d the resulting persilylated derivative was hydrolysed with methanol (6 cm^3). The solvent was evaporated to leave a crude residue which was purified by column chromatography to give the pulvinic acid (12 mg, 35%), m.p. 85–90 °C, λ_{max}(EtOH)/ nm 256 (ε 13 600), 286sh and 397 (ε 6900); λ_{max}(EtOH + 1 drop NaOH)/nm 298 (ε 19 700) and 418 (ε 5900); ν_{max}(KBr)/cm^{-1} 3400br m, 300br m, 2600br w, 1740m, 1675m, 1600s, 1365m, 1260m, 1180m, 1060m, 960m, 840m, 735m and 710m; δ_H([$^2H_6$]-acetone) 6.91 (d, *J* 9.0, 2 × aryl =CH), 7.42 (5 × =CH) and 8.03 (d, *J* 9.0, 2 × aryl =CH) (Found: M^+, 324.0589. $C_{18}H_{12}O_6$ requires *M*, 324.0630). An accurate combustion analysis could not be obtained for this compound.

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