The Structure and Synthesis of the Novel Orchid Pigments Dengibsin and Dengibsinin

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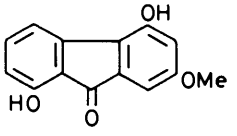
The structures of the orchid pigments dengibsin and dengibsinin have been revised to 2,5-dihydroxy-4-methoxy-9*H*-fluoren-9-one (**4**) and 3,5-dihydroxy-2,4-dimethoxy-9*H*-fluoren-9-one (**5**). The synthesis of these compounds is described. It has been found that 2′-methoxybiphenyl-2-carboxylic acids, on treatment with trifluoroacetic anhydride or oxalyl chloride, undergo cyclization giving 6*H*-dibenzo[*b*,*d*]pyran-6-ones.

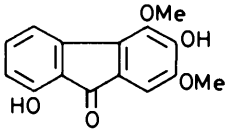
Recently Talapatra and co-workers [1] reported the isolation and structural determination of two fluorenones from the Asiatic orchid *Dendrobium gibsonii* Lindl. This is the first report of the natural occurrence of fluorenones. The Indian workers proposed on spectroscopic grounds structure (**1**) for dengibsin and structure (**2**) for dengibsinin. Both compounds give positive tests with iron(III) chloride and their ^{1}H n.m.r. spectra contain low-field 1 H singlets attributable to hydroxy groups; that in the spectrum of dengibsin occurring at δ 8.92 and that for dengibsinin at δ 9.14. The hydroxy group resonance for 1-hydroxyfluorenone (**3**) occurs at δ 8.42.[2] This evidence was taken to be indicative that dengibsin and dengibsinin were 1-hydroxyfluorenones, and their i.r. spectra were also alleged to support the presence of chelated carbonyl groups although no shift of the carbonyl stretching frequency occurred on diacetylation or dimethylation of dengibsin, and the shift to higher frequency was small in the case of dengibsinin.

The spectroscopic evidence advanced by Talapatra *et al.*[1] could equally well be interpreted in terms of structure (**4**) for dengibsin and structure (**5**) for dengibsinin. It is likely that the *peri*-hydroxy group in these 4-hydroxy-5-methoxyfluorenones would be intramolecularly hydrogen-bonded to the 5-methoxy group. Such is the case in a range of 9-methoxydibenzofuran-1-ols where the hydroxy resonance occurs at δ 8.21—9.08 [3] in their ^{1}H n.m.r. spectra, and the similar protons in 8-methoxy-1-naphthols resonate near δ 9.25,[4] a value close to those observed for the chelated hydroxy groups of dengibsin and dengibsinin.

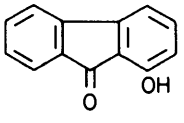
We first sought to synthesize compound (**2**) (see Scheme 1), the structure of which was proposed by Talapatra *et al.*[1] for dengibsinin. The readily available pyrogallol (**6**)[5] on isopropylation furnished the ether (**7**), which on bromination in acetic acid containing anhydrous sodium acetate smoothly gave the bromo compound (**8**). An excess of this bromo compound was caused to react in a crossed Ullmann reaction with the known bromo ester (**9**)[6] which afforded the biphenyl (**10**) in moderate yield. The derived acid (**11**) on cyclization with trifluoroacetic anhydride (TFAA) in dichloromethane at 0 °C furnished a high yield of the fluorenone (**12**). When compound (**12**) was treated with boron trichloride two products resulted: the desired diol (**2**) and the product (**13**) in which only deisopropylation had occurred. It was also observed that the methoxy group *para* to the carbonyl group in the di-*O*-methyl ether (**14**) of the putative dengibsinin (**2**) underwent demethylation when the compound was boiled with aqueous piperidine, and the hydroxyfluorenone (**13**), identical with that obtained by deisopropylation of compound (**12**), resulted. Similar selective demethylations have been recorded in the xanthone series.[7] Compound (**2**), its diacetate (**15**), its di-*O*-methyl ether (**14**), and its mono-*O*-methyl ether (**13**) all had different m.p.s and ^{1}H n.m.r. spectra to those recorded for



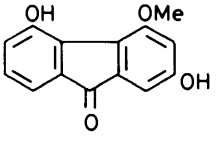
(**1**)



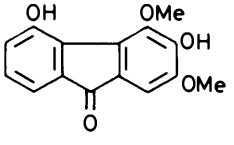
(**2**)



(**3**)



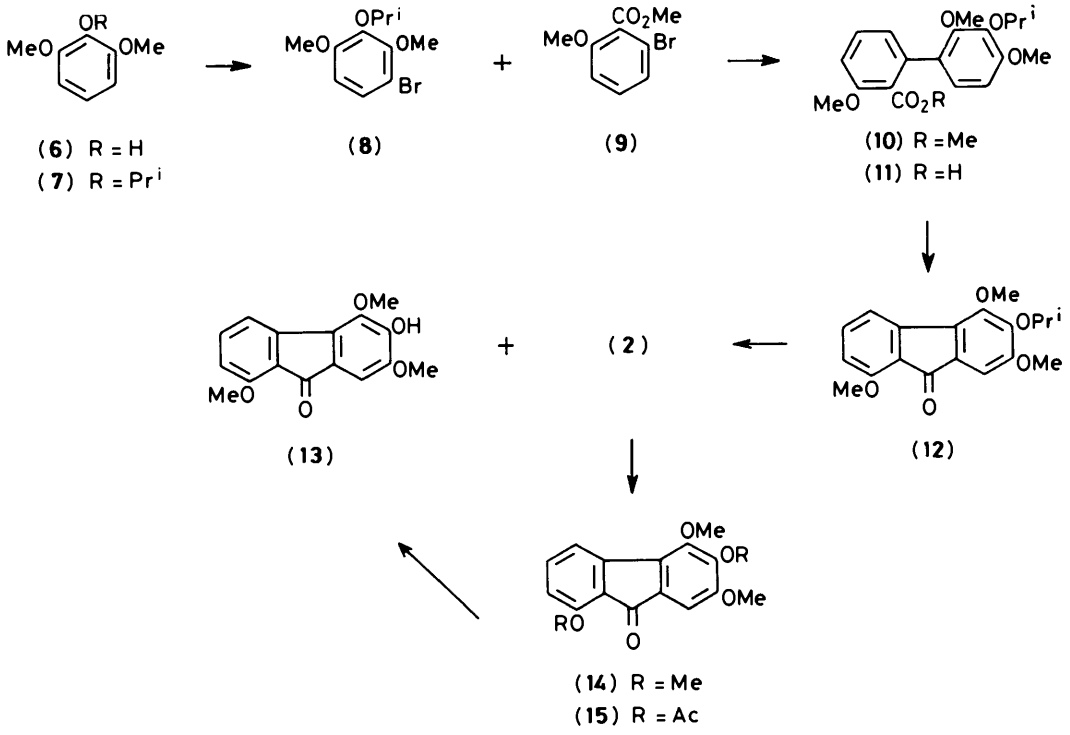
(**4**)



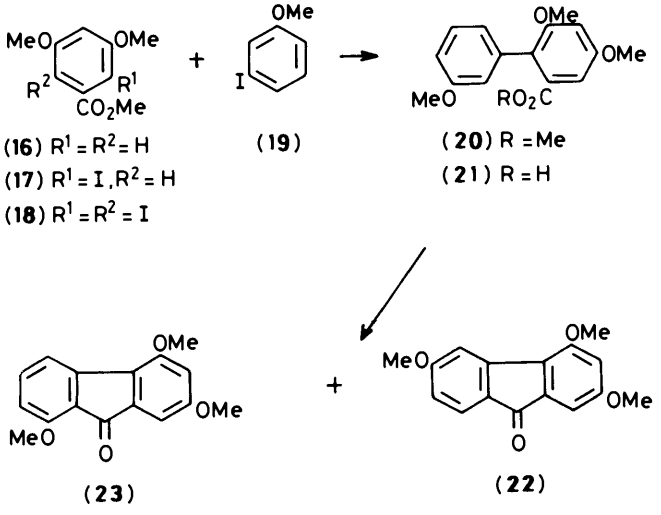
(**5**)

dengibsinin so that structure (**2**) cannot be correct for dengibsinin.

It now seemed likely that structure (**1**) was untenable for dengibsin. In order to establish this firmly it was decided to synthesize the derived di-*O*-methyl ether (**23**) (see Scheme 2). Iodination of methyl 3,5-dimethoxybenzoate (**16**) with a solution of iodine in chloroform in the presence of silver trifluoroacetate gave a mixture containing starting material, the desired mono iodo compound (**17**), and some di-iodo compound (**18**) which were separated by chromatography. The iodo compound (**17**) and an excess of 3-iodoanisole (**19**) were subjected to Ullmann reaction, and hydrolysis of the resultant ester (**20**) supplied the acid (**21**). Ring-closure in a similar manner to that used before gave a separable mixture of two fluorenones. The major product proved to be compound (**22**) in which cyclization had occurred *para* to the methoxy group, and the minor product (**23**) was that in which cyclization had occurred *ortho* to the methoxy group. The m.p. and ^{1}H n.m.r. spectrum of compound (**23**) were different to those recorded for the dengibsin derivative so that structure (**1**) for dengibsin is highly unlikely. It was therefore assumed that structures (**4**) and (**5**) were probably the correct structures for dengibsin and dengibsinin. In order to verify this proposal it was first decided to synthesize their di-*O*-methyl ethers. Thus Ullmann reaction (see Scheme 3) between the known bromo ester (**24**)[8] and an



Scheme 1.



Scheme 2.

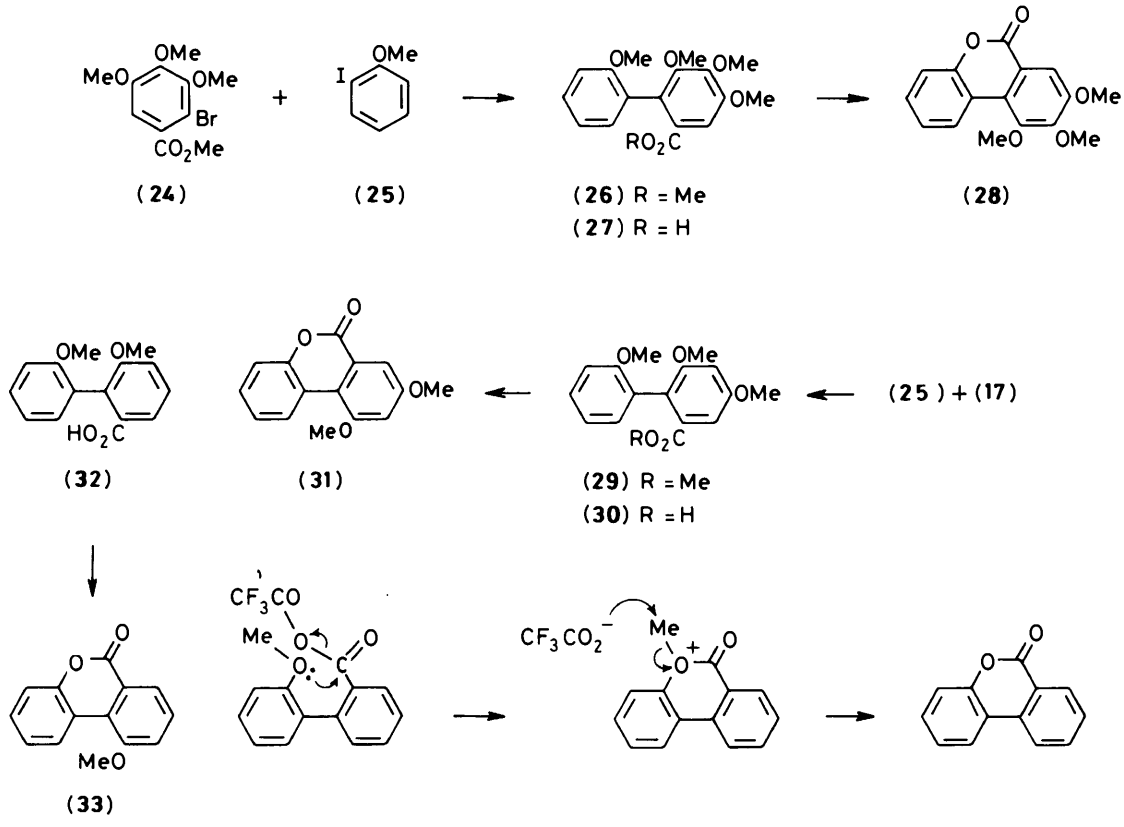
excess of 2-iodoanisole (**25**) yielded the ester (**26**) and thence the acid (**27**). However, on treatment with TFAA this acid furnished not a fluorenone but a compound that was formulated as the dibenzopyran (**28**) on the grounds of its spectroscopic and microanalytical data. Similarly the biphenylcarboxylic acid (**30**), prepared in a similar fashion, on treatment with oxalyl chloride gave the dibenzopyran (**31**), and the known biphenylcarboxylic acid (**32**)[9] gave the dibenzopyran (**33**) on treatment with TFAA. These biphenylcarboxylic acids are thus not sufficiently activated to undergo electrophilic substitution at the position *meta* to the methoxy group. Presumably the neighbouring methoxy group (Scheme 3) attacks the carbonyl group of the mixed anhydride formed from the biphenyl carboxylic acid and TFAA with the expulsion of trifluoroacetate. Trifluoroacetate then cleaves the methoxy group. A similar mechanism would operate for the acid chloride.

It is therefore apparent that the intermediate required for the synthesis of di-*O*-methyldengibsinin is the biphenylcarboxylic acid (**34**) since cyclization will be favoured by the *para*-methoxy group. The biphenylcarboxylic acid (**35**), however, possesses no such activating group and would not be expected to give di-*O*-methyldengibsin but a dibenzopyran on treatment with TFAA. A different strategy, disclosed in the sequel, must therefore be adopted for the synthesis of this compound. The biphenyl synthesis of Meyers[9] was adopted for the synthesis of the carboxylic acid (**34**) (see Scheme 4).

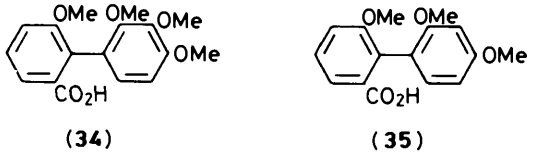
Thus an excess of the Grignard reagent (**37**) derived from 1-bromo-2,3,4-trimethoxybenzene[10] was allowed to react in tetrahydrofuran (THF) with the dihydro-oxazole (**36**)[9] and this gave a high yield of the biphenyl (**38**), which was quaternized with iodomethane; basic hydrolysis of the resultant salt afforded the required biphenylcarboxylic acid (**34**). On treatment with TFAA this compound gave the dibenzopyran (**39**) (56%) and the required fluorenone (**40**) (33%). When the fluorenone (**40**) was treated with boiling aqueous piperidine a high yield of the selectively demethylated product (**41**) was obtained, which on acetylation afforded the acetate (**42**). Compounds (**40**), (**41**), and (**42**) had ^{1}H n.m.r. spectra and m.p.s very similar to those reported for the analogous derivatives of dengibsinin so that structure (**5**) appears to be correct for the natural product.

In order to synthesize di-*O*-methyldengibsin the phenol (**41**) was treated with 5-chloro-1-phenyl-1*H*-tetrazole[11] and potassium carbonate in *N*,*N*-dimethylformamide (DMF) and the resultant tetrazolyl ether (**43**) was subjected to transfer hydrogenation.[12] A low yield of the trimethoxyfluorenone (**44**) was obtained and its properties agreed with those quoted for di-*O*-methyldengibsin so that structure (**4**) for dengibsin is likely.

It was argued that since Grignard reagents are able to displace a methoxy group *ortho* to a dihydro-oxazole moiety in, for example, compound (**36**), then an isopropoxy group should



Scheme 3.



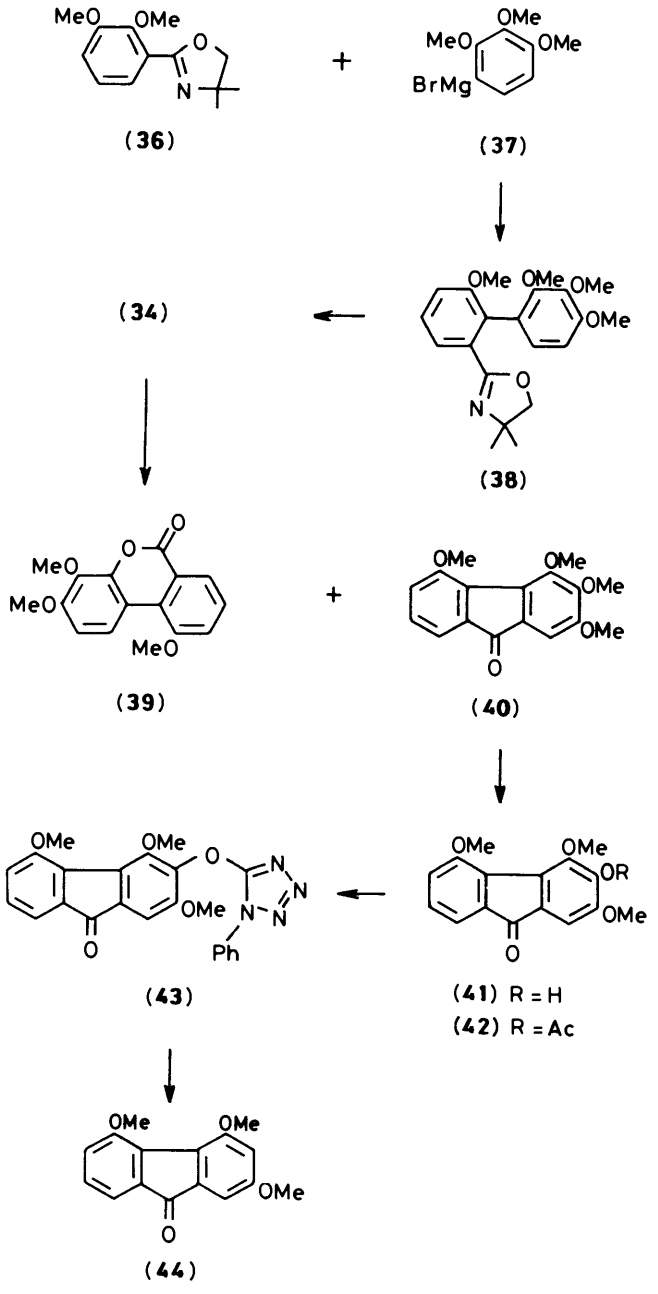
behave in the same way. Thus in order to synthesize dengibsinin (**5**) the dihydro-oxazole (**49**) was required (see Scheme 5). Consequently the known ester (**45**)[13] was converted into the ether (**46**) and the derived acid (**47**) was allowed to react with thionyl chloride at room temperature. The resultant acid chloride (**48**) was treated with 2-amino-2-methylpropan-1-ol and the crude amide, so obtained, on brief treatment with thionyl chloride gave the dihydro-oxazole (**49**). This was allowed to react with an excess of the Grignard reagent (**37**) derived from 1-bromo-2,3,4-trimethoxybenzene. The product was then converted into the biphenylcarboxylic acid (**50**) which was allowed to react with TFAA thereby providing a readily separable mixture of the dibenzopyran (**51**) and the fluorenone (**52**). Selective demethylation of the fluorenone (**52**) by boiling it with aqueous piperidine supplied the phenol (**53**). This latter compound on brief treatment with boron trichloride underwent deisopropylation and gave dengibsinin (**5**), and thence its diacetate (**54**). Although an authentic sample of dengibsinin was unobtainable the close agreement of the physical properties of the synthetic compound and four of its derivatives, recorded in this work, with those quoted in the literature[1] leave little doubt that structure (**5**) is correct.

In order to synthesize dengibsin (**4**) a route was adopted similar to that used in the synthesis of its di-*O*-methyl ether (**44**). The bromo compound (**66**) was therefore required (see Scheme 6). Bromination of methyl 2,3,4-trimethoxybenzoate (**55**)[14] gave a monobromo compound which was assigned structure (**56**) initially on the grounds of its ^{1}H n.m.r. spectrum which exhibited the aromatic proton as a singlet at δ 7.77. Compound (**56**) was different from its isomer (**63**), prepared by Sandmeyer reaction of the diazonium salt of the known amine (**62**).[15] In the ^{1}H n.m.r. spectrum of compound (**63**) the aromatic proton occurs as a singlet at higher field (δ 6.85). Treatment of the bromo ester (**56**) with boron trichloride gave the *ortho*-hydroxy ester (**57**), which on hydrolysis afforded the acid (**58**). On heating the acid (**58**) with copper(I) oxide and 2,2′-bipyridyl in *N*,*N*-dimethylaniline both decarboxylation and debromination occurred yielding the di-*O*-methylpyrogallol (**59**), so that this route to compound (**66**) was frustrated.

The di-*O*-methylpyrogallol (**59**) was more conveniently prepared by decarboxylation of 2-hydroxy-3,4-dimethoxybenzoic acid.[16] Bromination of the phenol (**59**) gave an inseparable mixture with composition 90% the *ortho*-*o*-bromophenol (**60**) and 10% the *p*-bromophenol (**61**). These structural assignments were made by comparison of the ^{1}H n.m.r. spectrum of the mixture with that of an authentic sample of compound (**60**) the preparation of which is described in the Experimental section. This route to compound (**66**) was also abandoned.

The di-*O*-methylpyrogallol (**59**) was converted into the isopropyl ether (**64**) and this on bromination provided a separable mixture of equal parts of the isomeric bromo compounds (**65**) and (**66**). The structures of these compounds were confirmed as follows.

The Grignard reagent of one of the isomers was carboxylated and the derived ester was treated with boron trichloride which yielded two products which were identified by their spectroscopic and microanalytical data as the esters (**68**) and



Scheme 4.

(**69**). The initial compound was therefore the isomer (**66**) and the intermediate ester was compound (**67**). These results were confirmed by NOESY experiments on the two isomers. In the spectrum of compound (**65**) there was a strong off-diagonal interaction between a methoxy resonance and an aromatic proton, thus demonstrating the proximity of these groups. In the spectrum of the isomer (**66**) there was no such interaction but a strong off-diagonal interaction between the aromatic protons. When compound (**65**) was treated with boron trichloride the *o*-bromophenol (**60**) resulted.

The Grignard reagent derived from the bromo compound (**66**) was allowed to react with the dihydro-oxazole (**49**) and the product was converted into the biphenylcarboxylic acid (**70**) (see Scheme 7). This on ring-closure afforded the dibenzopyran (**71**) and the fluorenone (**72**). Selective demethylation of the fluorenone gave the phenol (**73**), which was converted into the tetrazolyl ether (**74**). Hydrogenolysis of this last mentioned compound furnished a good yield of the fluorenone (**75**), which on deisopropylation with boron trichloride gave dengibsin (**4**), and thence its diacetate (**76**). No authentic sample of dengibsin could be obtained but again the correspondence between the physical properties of the synthetic compound and two of its derivatives with those of the natural product leaves little doubt that structure (**4**) is correct for dengibsin.

Talapatra *et al.*[1] suggest that the biosynthesis of dengibsin and dengibsinin might involve catabolism of phenanthrene precursors. Phenanthrenes are known to occur in the family Orchidaceae. Thus a 9,10-phenanthraquinone would undergo a benzil–benzilic acid shift followed by oxidative decarboxylation. It is of interest to note that the 9,10-dihydrophenanthrene (**77**), corresponding in structure to dengibsinin (**5**), has recently been isolated from an orchid.[17]

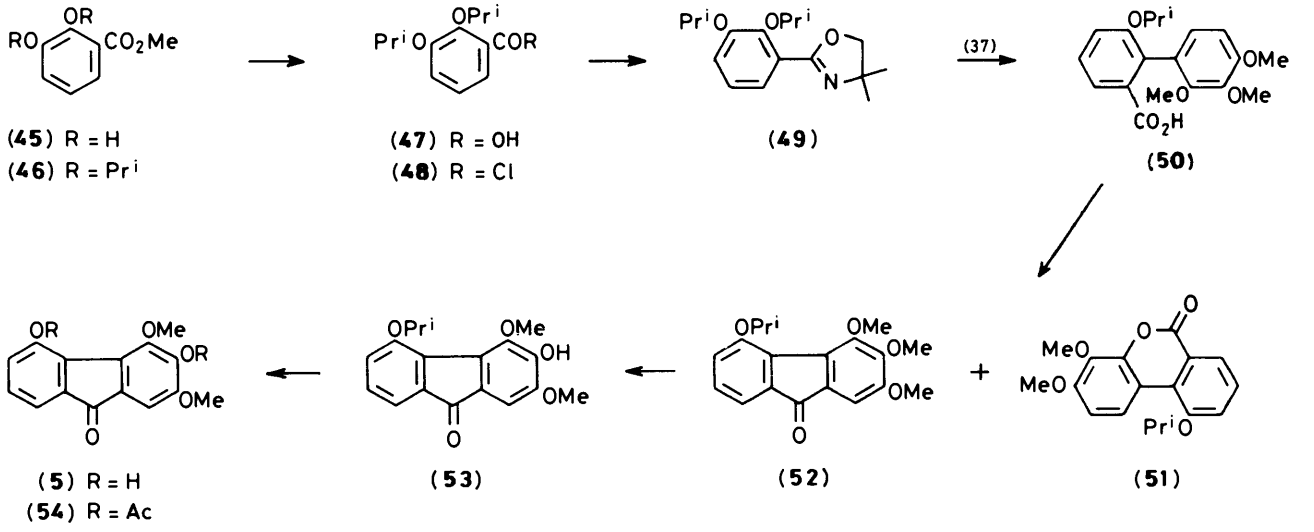
Experimental

M.p.s were determined on a Kofler hot-stage apparatus. Light petroleum was a fraction b.p. *ca.* 55—65 °C. All organic extracts were washed with saturated brine, and were then dried over anhydrous magnesium sulphate, prior to evaporation under reduced pressure. Radial chromatography was carried out on a Harrison Research Chromatotron with plates coated with Merck Kieselgel $60PF_{254}$. Silica gel was B.D.H. 60—120 mesh. ^1H N.m.r. spectra were recorded, unless stated otherwise for solutions in deuteriochloroform, at 60 MHz on a Hitachi-Perkin-Elmer R24 B instrument, at 80 MHz on a Bruker WP-80 spectrometer, or at 300 MHz on a Bruker AM-300 instrument. Mass spectra (35 eV) were recorded with a Hewlett-Packard 5986 instrument. I.r. spectra were recorded on a Perkin-Elmer 283 spectrophotometer, and electronic spectra for ethanolic solutions were measured with a Hewlett-Packard 8450A instrument.

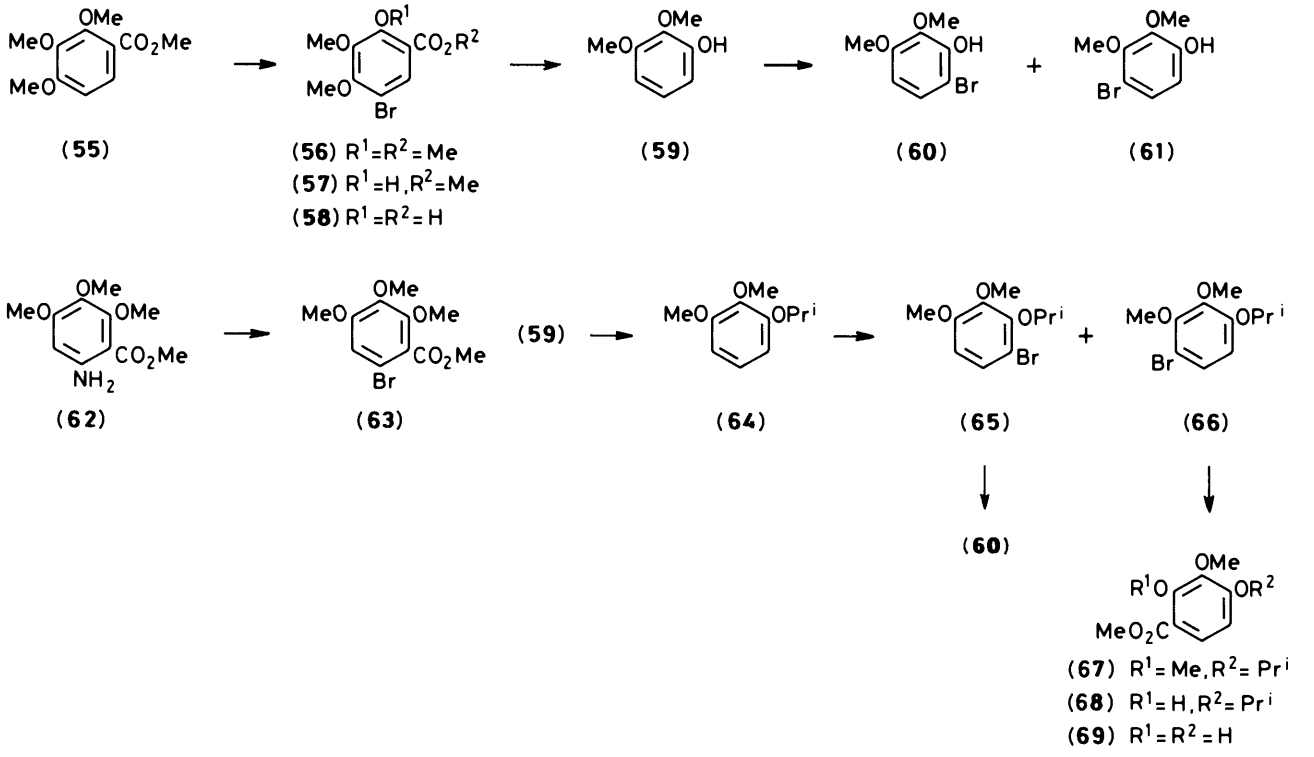
2-Isopropoxy-1,3-dimethoxybenzene (**7**).—A solution of 2,6-dimethoxyphenol (**6**) (17.8 g)[5] and 2-bromopropane (13.0 ml) in anhydrous DMF (75 ml) was stirred with anhydrous potassium carbonate (19.1 g) at 100 °C (bath) under dry nitrogen for 22 h. The suspension was poured into ice–water and the crude product was isolated with ether, then distilled under diminished pressure, and was obtained as an *oil* (14.7 g, 65%), b.p. 170 °C at 30 mmHg (Kugelrohr) (Found: C, 67.4; H, 8.3. $C_{11}H_{16}O_3$ requires C, 67.3; H, 8.2%); δ (60 MHz) 1.26 (6 H, d, Me_2CH), 3.72 (6 H, s, 2 × OMe), 4.28 (1 H, septet, $CHMe_2$), and 6.34—7.11 (3 H, m, ArH).

1-Bromo-3-isopropoxy-2,4-dimethoxybenzene (**8**).—A solution of bromine (6.5 g) in acetic acid (25 ml) was added dropwise to a stirred solution of the pyrogallol (**7**) (8.0 g) in acetic acid (30 ml) containing anhydrous sodium acetate (6.6 g). The mixture was next poured into water and the acetic acid was neutralized by the addition of solid sodium carbonate. The crude product was isolated with ethyl acetate and distilled under reduced pressure whereupon it was obtained as an *oil* (10.3 g, 92%), b.p. 120 °C at 0.3 mmHg (Kugelrohr) (Found: C, 48.1; H, 5.45; Br, 28.95%; M^+, 274/276. $C_{11}H_{15}BrO_3$ requires C, 48.0; H, 5.5; Br, 29.05%; *M*, 274/276).

Methyl 3′-Isopropoxy-2′,3,4′-trimethoxybiphenyl-2-carboxylate (**10**).—An intimate mixture of methyl 2-bromo-6-methoxybenzoate (**9**) (1.5 g),[6] the bromopyrogallol (**8**) (8.42 g), and freshly activated copper bronze (10.0 g) was heated under dry nitrogen at 240 °C (internal temperature) for 6 h. The cooled mixture was extracted exhaustively with boiling ethyl acetate and the crude product (7.5 g) was heated at 100 °C (bath) with potassium hydroxide (8.0 g), water (10 ml), and dimethyl



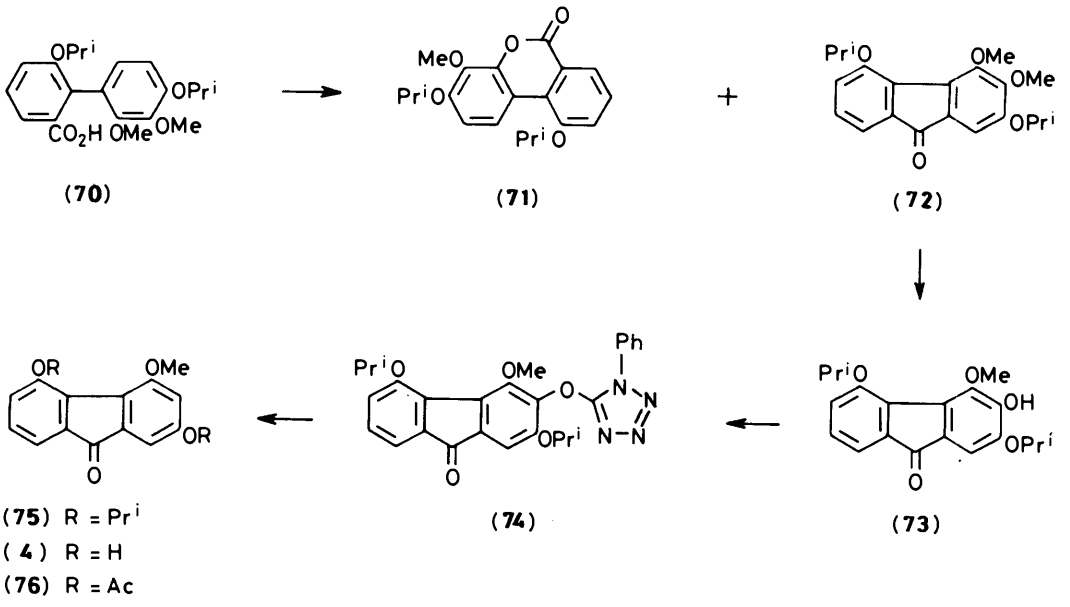
Scheme 5.



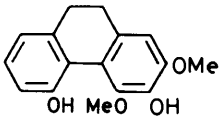
Scheme 6.

sulphoxide (50 ml) for 16 h. The solution was diluted with water and next extracted with ether (2 ×); these extracts were discarded. The aqueous phase was acidified with hydrochloric acid and the crude acidic product was isolated with ethyl acetate and methylated in the usual way with iodomethane and potassium carbonate in DMF. The crude ester was purified by radial chromatography with 10% ethyl acetate–light petroleum as eluant. This yielded the *ester* (**10**) (940 mg, 43%) as a gum, b.p. 195 °C at 0.005 mmHg (Kugelrohr) (Found: C, 66.8; H, 6.65%; M^+, 360. $C_{20}H_{24}O_6$ requires C, 66.85; H, 6.7%; *M*, 360); δ (80 MHz) 1.32 (6 H, d, Me_2CH), 3.58, 3.64, 3.85, and 3.88 (each 3 H, s, OMe), 4.46 (1 H, septet, $CHMe_2$), 6.64 and 6.88 (2 H, AB, *J* 8.6 Hz, 5′- and 6′-H), and 6.87—7.47 (3 H, m, 4-, 5-, and 6-H).

6-*Isopropoxy*-1,5,7-*trimethoxy*-9H-*fluoren*-9-*one* (**12**).—The ester (**10**) (832 mg) was hydrolysed as described above, and a solution of the crude acid in dichloromethane (15 ml) was stirred and cooled at 0 °C, and TFAA (1.0 ml) was added. The solution was stirred at 0 °C for 0.5 h and then poured into water. The crude product was extracted into ethyl acetate and the extract was washed successively with saturated aqueous sodium hydrogen carbonate and with saturated brine. The *fluorenone* (**12**) (727 mg, 96%) crystallized from dichloromethane–light petroleum as yellow blades, m.p. 110—111 °C (Found: C, 69.55; H, 6.1%; M^+, 328. $C_{19}H_{20}O_5$ requires C, 69.5; H, 6.15%; *M*, 328); δ (80 MHz) 1.48 (6 H, d, Me_2CH), 3.89, 3.97, and 3.99 (each 3 H, s, OMe), 4.54 (1 H, septet, $CHMe_2$), 6.69—7.42 (3 H, m, 2-, 3-, and 4-H), and 7.06 (1 H, s, 8-H).



Scheme 7.



(77)

1,6-*Dihydroxy*-5,7-*dimethoxy*-9H-*fluoren*-9-*one* (**2**) *and* 6-*Hydroxy*-1,5,7-*trimethoxy*-9H-*fluoren*-9-*one* (**13**).—A solution of the fluorenone (**12**) (710 mg) in dichloromethane (15 ml) was stirred at 0 °C and treated with a solution of boron trichloride (1.07 g) in dichloromethane (5 ml). After 1 h water was added and the crude product was isolated with dichloromethane and chromatographed over a column of silica gel with 10—30% ethyl acetate–light petroleum as eluant. The first band which was eluted supplied the *dihydroxyfluorenone* (**2**) (138 mg, 23%), which crystallized from dichloromethane–light petroleum as orange needles, m.p. 176—178 °C (Found: C, 66.05; H, 4.5%; M^+, 272. $C_{15}H_{12}O_5$ requires C, 66.15; H, 4.45%; *M*, 272); δ (300 MHz) 3.95 and 4.02 (each 3 H, s, OMe), 6.68 (1 H, dd, $J_{2,3}$ 8.4, $J_{2,4}$ 0.6 Hz, 2-H), 7.01 (1 H, s, 8-H), 7.19 (1 H, dd, $J_{4,3}$ 7.2, $J_{4,2}$ 0.6 Hz, 4-H), and 7.30 (1 H, dd, $J_{3,2}$ 8.4, $J_{3,4}$ 7.2 Hz, 3-H). The *di-O-methyl ether* (**14**), prepared by methylation with iodomethane and potassium carbonate in DMF at room temperature, formed deep yellow plates (from dichloromethane–light petroleum), m.p. 154—155 °C (Found: C, 68.1; H, 5.35%; M^+, 300. $C_{17}H_{16}O_5$ requires C, 68.0; H, 5.35%; *M*, 300); δ (300 MHz) 3.92, 3.94, 3.95, and 4.00 (each 3 H, s, OMe), 6.76 (1 H, dd, $J_{2,3}$ 8.3, $J_{2,4}$ 0.9 Hz, 2-H), 7.06 (1 H, s, 8-H), 7.34 (1 H, dd, $J_{4,3}$ 7.3, $J_{4,2}$ 1.0 Hz, 4-H), and 7.40 (1 H, dd, $J_{3,2}$ 8.3, $J_{3,4}$ 7.3 Hz, 3-H). The *diacetate* (**15**) formed yellow needles (from dichloromethane–light petroleum), m.p. 161—163 °C (Found: C, 64.35; H, 4.75%; M^+, 356. $C_{19}H_{16}O_7$ requires C, 64.05; H, 4.55%; *M*, 356); δ (300 MHz) 2.42 and 2.39 (each 3 H, s, MeCO), 3.87 and 3.94 (each 3 H, s, OMe), 6.85 (1 H, dd, $J_{2,3}$ 8.1, $J_{2,4}$ 0.9 Hz, 2-H), 7.06 (1 H, s, 8-H), 7.46 (1 H, dd, $J_{3,2}$ 8.1, $J_{3,4}$ 7.5 Hz, 3-H), and 7.61 (1 H, dd, $J_{4,3}$ 7.5, $J_{4,2}$ 0.9 Hz, 4-H).

Further elution of the column afforded the *hydroxyfluorenone* (**13**) (259 mg, 42%), which formed hexagonal orange plates (from ethyl acetate), m.p. 204—206 °C (Found: C, 67.3; H, 4.95%; M^+, 286. $C_{16}H_{14}O_5$ requires C, 67.15; H, 4.95%; *M*, 286); δ (300 MHz) 3.95, 3.97, and 4.01 (each 3 H, s, OMe), 5.99 (1 H, s, OH), 6.77 (1 H, dd, $J_{2,3}$ 8.0, $J_{2,4}$ 1.3 Hz, 2-H), 7.04 (1 H, s, 8-H), 7.27 (1 H, dd, $J_{4,3}$ 7.3, $J_{4,2}$ 1.3 Hz, 4-H), and 7.40 (1 H, dd, $J_{3,2}$ 8.0, $J_{3,4}$ 7.3 Hz, 3-H).

Demethylation of 1,5,6,7-*Tetramethoxy*-9H-*fluoren*-9-*one* (**14**).—A solution of the fluorenone (**14**) (81.0 mg) in piperidine (10 ml) and water (5 ml) was boiled and stirred under reflux under nitrogen for 12 h. The cooled solution was acidified with dil. hydrochloric acid and the crude product was isolated with ethyl acetate; it crystallized from ethyl acetate as hexagonal orange plates (65 mg, 84%) of the hydroxyfluorenone (**13**), m.p. and mixed m.p. 204—206 °C.

Iodination of Methyl 3,5-*Dimethoxybenzoate* (**16**).—A solution of iodine (5.18 g) in chloroform (200 ml) was added slowly dropwise to a stirred solution of the substrate (**16**) (4.00 g) in chloroform (50 ml) containing suspended silver trifluoroacetate (4.51 g). After the addition the precipitated silver iodide was collected by filtration and washed with dichloromethane. The combined filtrate and washings were washed in turn with water, saturated aqeuous sodium hydrogen carbonate solution, aqueous sodium thiosulphate, and finally with saturated brine. The crude product was chromatographed over silica gel with 10% ethyl acetate–light petroleum as eluant. Early fractions afforded some starting material which was followed by *methyl* 2-*iodo*-3,5-*dimethoxybenzoate* (**17**), which formed plates (3.2 g, 49%) (from dichloromethane–light petroleum), m.p. 80—81 °C (Found: C, 37.35; H, 3.4; I, 39.4%; M^+, 322. $C_{10}H_{11}IO_4$ requires C, 37.3; H, 3.45; I, 39.4%; *M*, 322); δ (80 MHz) 3.83, 3.88, and 3.93 (each 3 H, s, OMe) and 6.52 and 6.81 (2 H, AB, *J* 2.7 Hz, ArH). Further elution afforded *methyl* 2,6-*di-iodo*-3,5-*dimethoxybenzoate* (**18**), which crystallized from dichloromethane–light petroleum as laths (2.1 g, 23%), m.p. 155—157 °C (Found: C, 26.9; H, 2.25; I, 56.55. $C_{10}H_{10}I_2O_4$ requires C, 26.8; H, 2.25; I, 56.65%); δ (80 MHz) 3.90 (6 H, s, 2 × OMe), 3.98 (3 H, s, OMe), and 6.38 (1 H, s, ArH).

Methyl 3′,4,6-*Trimethoxybiphenyl*-2-*carboxylate* (**20**).—Ullmann reaction between 3-iodoanisole (**19**) (3.6 g) and methyl 2-iodo-3,5-dimethoxybenzoate (**17**) (1.0 g) in a manner similar to that described for the preparation of compound (**10**) supplied the *biphenyl* (**20**) as a thick oil (351 mg, 37%) (Found: C, 67.7; H,

6.25%; M^+, 302. $C_{17}H_{18}O_5$ requires C, 67.55; H, 6.0%; M, 302): δ (300 MHz) 3.55, 3.74, 3.80, and 3.87 (each 3 H, s, OMe), 6.65 and 6.87 (2 H, AB, $J_{3,5}$ 2.4 Hz, 5- and 3-H), 6.80—6.89 (3 H, m, ArH), and 7.25—7.31 (1 H, m, ArH).

2,4,6-*Trimethoxy*-9H-*fluoren*-9-*one* (**22**) *and* 1,5,7-*Trimethoxy*-9H-*fluoren*-9-*one* (**23**).—Hydrolysis and ring-closure of the ester (**20**) (292 mg) in a manner similar to that described for the preparation of compound (**12**) afforded a crude product, which was chromatographed over silica gel with 20% ethyl acetate–light petroleum as eluant. The first band which was eluted supplied 2,4,6-*trimethoxy*-9H-*fluoren*-9-*one* (**22**) (160 mg, 61%), which crystallized from dichloromethane–light petroleum as yellow needles, m.p. 190—192 °C (Found: C, 70.85; H, 5.45%; M^+, 270. $C_{16}H_{16}O_4$ requires C, 71.1; H, 5.2%; M, 270); δ (300 MHz, assignments by spin decoupling) 3.85, 3.89, and 3.92 (each 3 H, s, OMe), 6.53 and 6.82 (2 H, AB, $J_{1,3}$ 2.1 Hz, 3- and 1-H), 6.58 (1 H, dd, $J_{7,8}$ 8.2, $J_{7,5}$ 2.3 Hz, 7-H), 7.21 (1 H, d, $J_{5,7}$ 2.3 Hz, 5-H), and 7.52 (1 H, d, $J_{8,7}$ 8.2 Hz, 8-H).

Further elution afforded 1,5,7-*trimethoxy*-9H-*fluoren*-9-*one* (**23**) (35 mg, 13%), which crystallized from methanol as rosettes of orange needles, m.p. 137—139 °C (Found: C, 71.0; H, 5.6%; M^+, 270); δ (300 MHz) 3.86, 3.93, and 3.97 (each 3 H, s, OMe), 6.54 and 6.85 (2 H, AB, $J_{6,8}$ 2.1 Hz, 6- and 8-H), 6.71 (1 H, dd, $J_{2,3}$ 7.9, $J_{2,4}$ 1.2 Hz, 2-H), 7.33 (1 H, dd, $J_{4,3}$ 7.4, $J_{4,2}$ 1.2 Hz, 4-H), and 7.38 (1 H, dd, $J_{3,2}$ 7.9, $J_{3,4}$ 7.4 Hz, 3-H).

Methyl 2′,4,5,6-*Tetramethoxybiphenyl*-2-*carboxylate* (**26**).—Ullmann reaction between 2-iodoanisole (**25**) (5.75 g) and methyl 2-bromo-3,4,5-trimethoxybenzoate (**24**) (1.5 g)[8] in a manner similar to that described for the preparation of compound (**10**) yielded the biphenyl (**26**) (243 mg, 11%) as a thick oil (Found: C, 65.1; H, 5.8%; M^+, 332. $C_{18}H_{20}O_6$ requires C, 65.05; H, 6.05%; M, 332).

8,9,10-*Trimethoxy*-6H-*dibenzo*[b,d]*pyran*-6-*one* (**28**).—The ester (**26**) (230 mg) was hydrolysed in a manner similar to that described in the preparation of compound (**12**). A solution of the crude acid (**27**) in dichloromethane (5 ml) was stirred and treated at 0 °C with TFAA (0.5 ml) and the solution was stirred at room temperature for 4 h, diluted with ethyl acetate, and washed in turn with saturated aqueous sodium hydrogen carbonate and with saturated brine. The crude product crystallized from dichloromethane–light petroleum as needles (139 mg, 70%) of the *dibenzopyran* (**28**), m.p. 158—159 °C (Found: C, 67.1; H, 5.1%; M^+, 286. $C_{16}H_{14}O_5$ requires C, 67.15; H, 4.95%; M, 286); δ (300 MHz, assignments by spin decoupling) 3.99, 4.00, and 4.05 (each 3 H, s, OMe), 7.32 (1 H, ddd, $J_{2,1}$ 8.3, $J_{2,3}$ 7.7, $J_{2,4}$ 1.7 Hz, 2-H), 7.36 (1 H, dd, $J_{4,3}$ 7.7, $J_{4,2}$ 1.7 Hz, 4-H), 7.44 (1 H, ddd, $J_{3,4}$ 7.7, $J_{3,2}$ 7.7, $J_{3,2}$ 1.5 Hz, 3-H), 7.77 (1 H, s, 7-H), and 8.85 (1 H, dd, $J_{1,2}$ 8.3, $J_{1,3}$ 1.5 Hz, 1-H).

Methyl 2′,4,6-*Trimethoxybiphenyl*-2-*carboxylate* (**29**).—Ullmann reaction between 2-iodoanisole (**25**) (4.4 g) and methyl 2-iodo-3,5-dimethoxybenzoate (**17**) (1.0 g) in a manner similar to that described for the preparation of compound (**10**) supplied the *biphenyl* (**29**) (164 mg, 17%) as a thick oil (Found: C, 67.5; H, 6.1%; M^+, 302. $C_{17}H_{18}O_5$ requires C, 67.55; H, 6.0%; M, 302).

8,10-*Dimethoxy*-6H-*dibenzo*[b,d]*pyran*-6-*one* (**31**).—Hydrolysis of the ester (**29**) (142 mg) in a manner similar to that described in the preparation of compound (**12**) gave the crude acid (**30**), which was dissolved in dichloromethane (8 ml) and the solution was stirred at room temperature with oxalyl chloride (2.0 ml) during 3 h. The usual work-up afforded the *dibenzopyran* (**31**) (109.5 mg, 91%), which crystallized from dichlormethane–light petroleum as needles, m.p. 205—206 °C (Found: C, 70.4; H, 4.75%; M^+, 256. $C_{15}H_{12}O_4$ requires C, 70.3; H, 4.7; M, 256); δ (300 MHz, assignments by spin decoupling) 3.94 and 4.03 (each 3 H, s, OMe), 6.90 (1 H, d, $J_{9,7}$ 2.6 Hz, 9-H), 7.29 (1 H, ddd, $J_{2,1}$ 8.9, $J_{2,3}$ 7.4, $J_{2,4}$ 1.8 Hz, 2-H), 7.34 (1 H, dd, $J_{4,3}$ 7.8, $J_{4,2}$ 1.8 Hz, 4-H), 7.40 (1 H, ddd, $J_{3,4}$ 7.8, $J_{3,2}$ 7.4, $J_{3,1}$ 1.5 Hz, 3-H), 7.53 (1 H, d, $J_{7,9}$ 2.6 Hz, 7-H), and 8.86 (1 H, dd, $J_{1,2}$ 8.9, $J_{1,3}$ 1.5 Hz, 1-H).

10-*Methoxy*-6H-*dibenzo*[b,d]*pyran*-6-*one* (**33**).—Ring-closure of 2′,6-dimethoxybiphenyl-2-carboxylic acid (**32**)[9] with TFAA during 4 h in a manner similar to that described for the preparation of compound (**12**) yielded the *dibenzopyran* (**33**) (40%), which crystallized from methanol as felted needles, m.p. 126—127 °C (Found: C, 74.15; H, 4.55%; M^+, 226. $C_{14}H_{10}O_3$ requires C, 74.3; H, 4.45%; M, 226); δ (80 MHz) 4.04 (3 H, s, OMe), 7.22—7.59 (5 H, m, ArH), 8.05 (1 H, dd, $J_{7,8}$ 7.5, $J_{7,9}$ 1.6 Hz, 7-H), and 8.90 (1 H, m, 1-H).

2,3,4,5-*Tetramethoxy*-9H-*fluoren*-9-*one*(*Di*-O-*methyldengibsinin*) (**40**) *and* 3,4,10-*Trimethoxy*-6H-*dibenzo*[b,d]*pyran*-6-*one* (**39**).—The Grignard reagent (**37**) was prepared in the usual way under dry nitrogen from 1-bromo-2,3,4-trimethoxybenzene (9.0 g),[10] magnesium (0.9 g), and THF (40 ml). The Grignard reagent was next added in a thin stream to a stirred solution of 2-(2,3-dimethoxyphenyl)-4,5-dihydro-4,4-dimethyloxazole (**36**) (5.0 g)[9] in anhydrous THF (60 ml) under dry nitrogen at room temperature. The mixture was stirred at room temperature for 3 h and then poured into water and extracted with ethyl acetate. The extract was washed with water and then exhaustively extracted with dil. hydrochloric acid. The acidic extracts were basified with dil. aqueous sodium hydroxide and the crude product was isolated with ethyl acetate. The dihydro-oxazole (**38**) was obtained as a viscous oil (7.8 g, 99%); δ (80 MHz) 1.17 and 1.18 (each 3 H, s, CMe_2), 3.68, 3.76, 3.88, and 3.89 (each 3 H, s, OMe), 6.64 and 6.82 (2 H, AB, J 8.6 Hz, ArH), and 6.96—7.37 (3 H, m, ArH).

A portion of this dihydro-oxazole (**38**) (3.7 g), nitromethane (10 ml), and iodomethane (5 ml) were stirred and heated at 60 °C (bath) for 22 h. The solvents were removed under reduced pressure and the residue was stirred and heated under reflux with sodium hydroxide (20 g) in a mixture of methanol (100 ml) and water (100 ml) for 46 h. Most of the methanol was removed by distillation, the residue was diluted with water and extracted with ether, and the extract was discarded. The aqueous phase was acidified with dil. hydrochloric acid and the crude acid (**34**) was isolated with ethyl acetate. The extract was washed in turn with water, aqueous sodium thiosulphate, and finally with saturated brine. The crude acid was dissolved in dichloromethane (20 ml) and the solution was stirred and treated with TFAA (4.0 ml), then stirred at room temperature for 6.5 h. Work-up in the customary way gave a crude product, which was chromatographed over silica gel with 10—30% ethyl acetate–light petroleum as eluant. Early fractions afforded *di*-O-*methyldengibsinin* (**40**), which formed orange rods (1.0 g, 33%) from methanol, m.p. 127—128 °C (lit.,[1] 110 °C)* (Found: C, 68.25; H, 5.3%; M^+, 300. $C_{17}H_{16}O_5$ requires C, 68.0; H, 5.35%; M, 300); δ (300 MHz) 3.90, 3.92, 3.96, and 3.98 (each 3 H, s, OMe), 7.07 (1 H, dd, $J_{6,7}$ 8.1, $J_{6,8}$ 1.1 Hz, 6-H), 7.12 (1 H, s, 1-H), 7.21 (1 H, dd, $J_{7,6}$ 8.1, $J_{7,8}$ 7.1 Hz, 7-H), and 7.28 (1 H, dd, $J_{8,7}$ 7.1, $J_{8,6}$ 1.1 Hz, 8-H); $\lambda_{max.}$ 276, 339, 354, and 434 nm (ε 40 900, 7 300, 7 300, and 3 100 respectively). Further elution of the above column yielded the *dibenzopyran* (**39**), which crystallized from methanol as felted needles (1.6 g, 56%), m.p. 139—140 °C (Found: C, 67.1; H, 4.9%; M^+, 286. $C_{16}H_{14}O_5$ requires C, 67.15; H, 4.95%; M, 286); δ (300 MHz) 3.96, 3.99, and 4.04 (each 3 H, s, OMe), 6.86 (1 H, d, $J_{2,1}$ 9.4 Hz, 2-H), 7.28 (1 H, dd, $J_{9,7}$ 1.1, $J_{9,8}$ 8.1 Hz, 9-H), 7.43 (1 H, dd, $J_{8,7}$ 8.0, $J_{8,9}$ 8.1 Hz,

* Lit. m.p. for compound erroneously assigned structure (**14**).

8-H), 7.90 (1 H, dd, $J_{7,8}$ 8.0, $J_{7,9}$ 1.1 Hz, 7-H), and 8.63 (1 H, d, $J_{1,2}$ 9.4 Hz, 1-H).

3-*Hydroxy*-2,4,5-*trimethoxy*-9H-*fluoren*-9-*one* (**41**).—Di-*O*-methyldengibsinin (**40**) (430 mg), piperidine (25 ml), and water (5 ml) were heated and stirred under reflux for 17 h. The solution was cooled and acidified with dil. hydrochloric acid. The crude product was isolated with ethyl acetate. The *hydroxyfluorenone* (**41**) (370 mg, 90%) crystallized from methanol as orange plates, m.p. 215—217 °C (lit.,[1] 205 °C)* (Found: C, 67.05; H, 4.85%; M^+, 286. $C_{16}H_{14}O_5$ requires C, 67.15; H, 4.95%; *M*, 286); δ (300 MHz) 3.89, 3.95, and 3.98 (each 3 H, s, OMe), 6.16 (1 H, s, OH), 7.07 (1 H, dd, $J_{6,7}$ 8.0, $J_{6,8}$ 1.3 Hz, 6-H), 7.12 (1 H, s, 1-H), 7.22 (1 H, dd, $J_{7,6}$ 8.0, $J_{7,8}$ 7.1 Hz, 7-H), and 7.28 (1 H, dd, $J_{8,7}$ 7.1, $J_{8,6}$ 1.3 Hz, 8-H); $\lambda_{max.}$ 283, 322, and 365 nm (ε 34 600, 4 500, and 6 000 respectively); $\lambda_{max.}$ (EtOH + NaOH) 261, 310, 406, and 512 nm (ε 19 700, 25 200, 7 700, and 3 700 respectively). The *acetate* (**42**) crystallized from methanol as orange needles, m.p. 145—146 °C (lit.,[1] 140 °C)† (Found: C, 65.9; H, 4.9%; M^+, 328. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.9%; *M*, 328); δ (300 MHz) 2.38 (3 H, s, MeCO), 3.82, 3.89, and 3.95 (each 3 H, s, OMe), 7.07 (1 H, dd, $J_{6,7}$ 8.1, $J_{6,8}$ 1.1 Hz, 6-H), 7.17 (1 H, s, 1-H), 7.22 (1 H, dd, $J_{7,6}$ 8.1, $J_{7,8}$ 7.1 Hz, 7-H), and 7.29 (1 H, dd, $J_{8,7}$ 7.1, $J_{8,6}$ 1.1 Hz, 8-H); $\lambda_{max.}$ 265, 273, 306, 337, 346, and 444 nm (ε 43 200, 47 100, 3 600, 4 400, 4 200, and 1 500 respectively).

2,4,5-*Trimethoxy*-3-(1-*phenyltetrazol*-5-*xyloxy*)-9H-*fluoren*-9-*one* (**43**).—The hydroxyfluorenone (**41**) (372 mg), 5-chloro-1-phenyltetrazole (243 mg), and potassium carbonate (2.0 g) were stirred and heated under dry nitrogen in anhydrous DMF (10 ml) at 80 °C (bath) for 5 h when a further quantity of the tetrazole (200 mg) was added and the mixture was heated and stirred for a further 16 h. The mixture was poured into water and the crude product was isolated with ethyl acetate and purified by radial chromatography with 30% ethyl acetate–light petroleum as eluant. The *tetrazole* (**43**) (519 mg, 93%) crystallized from methanol as orange needles, m.p. 199—200 °C (Found: C, 64.05; H, 4.15; N, 13.05%; M^+, 430. $C_{23}H_{18}N_4O_5$ requires C, 64.2; H, 4.2; N, 13.0%; *M*, 430); δ (80 MHz) 3.79, 3.86, and 3.94 (each 3 H, s, OMe) and 7.15—7.96 (9 H, m, ArH).

2,4,5-*Trimethoxy*-9H-*fluoren*-9-*one* (*Di*-O-*methyldengibsin*) (**44**).—The tetrazole (**43**) (205 mg) and palladium–charcoal (Engelhard; 10%; 240 mg) were stirred in a mixture of water (6 ml), ethanol (9 ml), and benzene (21 ml); hydrazine hydrate (98%; 3 ml) was added and the mixture was stirred at room temperature for 2 h, whereupon a further quantity (3 ml) of hydrazine hydrate was added. After 3 h the catalyst was separated by filtration and washed with ethyl acetate. The filtrate was washed in turn with water, dil. hydrochloric acid, and finally with saturated brine. The crude product contained much starting material and it was extracted with boiling light petroleum (3 × 100 ml). The extract was purified by radial chromatography with 20% ethyl acetate–light petroleum as eluant which yielded the *dengibsin* (**44**) (11.7 mg, 9%), which formed red needles (from dichloromethane–light petroleum), m.p. 134—136 °C (lit.,[1] 122 °C)‡ (Found: C, 71.35; H, 5.25%; M^+, 270. $C_{16}H_{14}O_4$ requires C, 71.1; H, 5.2%; *M*, 270); δ (300 MHz) 3.86, 3.91, and 3.92 (each 3 H, s, OMe), 6.60 (1 H, d, $J_{3,1}$ 2.3 Hz, 3-H), 6.91 (1 H, d, $J_{1,3}$ 2.3 Hz, 1-H), 7.06 (1 H, dd, $J_{6,7}$ 8.2, $J_{6,8}$ 1.1 Hz, 6-H), 7.16 (1 H, dd, $J_{7,6}$ 8.2, $J_{7,8}$ 7.1 Hz, 7-H), and 7.30 (1 H, dd, $J_{8,7}$ 7.1, $J_{8,6}$ 1.1 Hz, 8-H); $\lambda_{max.}$ 274, 337, 468, and 486 nm (ε 40 600, 5 000, 2 200, and 2 000 respectively).

Methyl 2,3-*Di-isopropoxybenzoate* (**46**).—Methyl 2,3-dihydroxybenzoate (**45**) (12.8 g),[13] 2-bromopropane (18.0 ml), and anhydrous potassium carbonate (26.5 g) were stirred together in anhydrous DMF (50 ml) at 80 °C (bath) under dry nitrogen for 18 h. The mixture was poured into water and isolation with ether gave the crude product as an oil, which was distilled under diminished pressure to give the *ester* (**46**) (18.0 g, 94%), b.p. 150 °C at 0.3 mmHg (Kugelrohr) (Found: C, 66.85; H, 7.95%; M^+, 252. $C_{14}H_{20}O_4$ requires C, 66.65; H, 8.0%; *M*, 252); δ (80 MHz) 1.28 and 1.33 (each 6 H, d, 2 × Me_2 CH), 3.88 (3 H, s, OMe), 4.52 and 4.54 (each 1 H, septet, C*H*Me$_2$), and 6.91—7.36 (3 H, m, ArH).

2-(2,3-*Di-isopropoxyphenyl*)-4,5-*dihydro*-4,4-*dimethyloxazole* (**49**).—Hydrolysis of the foregoing ester (**46**) (17.2 g) with aqueous methanolic potassium hydroxide in the customary way gave the crude acid (**47**) (16.1 g), which was stirred at room temperature with thionyl chloride (15 ml) for 22 h. The excess of thionyl chloride was removed under reduced pressure and finally by azeotropic distillation with tetrachloromethane. The crude acid chloride (**48**) was dissolved in dichloromethane (50 ml) and the solution was added dropwise to a stirred solution of 2-amino-2-methylpropan-1-ol (12.0 g) in dichloromethane (25 ml) at 0 °C. After the mixture had been stirred at room temperature for 1.5 h the precipitated hydrochloride was separated by filtration and washed with dichloromethane. Evaporation of the solvent gave the amide as a viscous gum, which was dissolved in dichloromethane (15 ml) and stirred at 0 °C during the dropwise addition of thionyl chloride (15 ml). The solution was stirred at room temperature for 1.25 h and diluted with ethyl acetate and next poured onto ice–water. The aqueous layer was separated and basified with dil. sodium hydroxide solution. The crude product was isolated with ethyl acetate and then distilled under reduced pressure to yield the *dihydro-oxazole* (**49**) (17.7 g, 90%) as an oil, b.p. 140 °C at 0.5 mmHg (Kugelrohr) (Found: C, 70.3; H, 8.4. $C_{17}H_{25}NO_3$ requires C, 70.05; H, 8.65%); δ (80 MHz) 1.26 and 1.31 (each 6 H, d, 2 × Me_2CH), 1.38 (6 H, s, Me_2C), 4.08 (2 H, s, CH_2), 4.47 (2 H, superimposed septets, 2 × C*H*Me$_2$), and 6.95—7.34 (3 H, m, ArH).

5-*Isopropoxy*-2,3,4-*trimethoxy*-9H-*fluoren*-9-*one* (**52**) *and* 10-*Isopropoxy*-3,4-*dimethoxy*-6H-*dibenzo*[b,d]*pyran*-6-*one* (**51**).—The Grignard reagent (**37**) prepared from 1-bromo-2,3,4-trimethoxybenzene (6.1 g) was allowed to react with the foregoing dihydro-oxazole (**49**) (4.3 g) and the same sequence of reactions was applied to the product as that described in the synthesis of compounds (**39**) and (**40**). The crude product was chromatographed over silica gel with 10—30% ethyl acetate–light petroleum as eluant. Early fractions afforded the *fluorenone* (**52**) (1.18 g, 24%) as a thick orange oil, b.p. 170 °C at 0.01 mmHg (Kugelrohr) (Found: C, 69.4; H, 6.25. $C_{19}H_{20}O_5$ requires C, 69.5; H, 6.15%).

Further elution yielded the *dibenzopyran* (**51**) (2.295 g, 49%), which crystallized from methanol as needles, m.p. 117—118 °C (Found: C, 68.9; H, 5.7%; M^+, 314. $C_{18}H_{18}O_5$ requires C, 68.8; H, 5.75%; *M*, 314); δ (300 MHz) 1.51 (6 H, d, Me_2CH), 3.97 and 4.00 (each 3 H, s, OMe), 4.81 (1 H, septet. C*H*Me$_2$), 6.90 (1 H, d, $J_{2,1}$ 9.4 Hz, 2-H), 7.31 (1 H, dd, $J_{9,8}$ 7.8, $J_{9,7}$ 1.3 Hz, 9-H), 7.43 (1 H, dd, $J_{8,7}$ 8.2, $J_{8,9}$ 7.8 Hz, 8-H), 8.03 (1 H, dd, $J_{7,8}$ 7.8, $J_{7,9}$ 1.3 Hz, 7-H), and 8.83 (1 H, d, $J_{1,2}$ 9.4 Hz, 1-H).

3-*Hydroxy*-5-*isopropoxy*-2,4-*dimethoxy*-9H-*fluoren*-9-*one* (**53**).—The fluorenone (**52**) (1.079 g) was boiled and stirred under reflux under dry nitrogen with piperidine (45 ml) and

* Lit. m.p. for compound erroneously assigned as 6-hydroxy-1,5,7-trimethoxy-9*H*-fluoren-9-one.

† Lit. m.p. for compound erroneously assigned as 6-acetoxy-1,5,7-trimethoxy-9*H*-fluoren-9-one.

‡ Lit. m.p. for compound erroneously assigned as structure (**23**).

water (10 ml) for 12 h. Work-up as described for compound (**41**) gave the *hydroxyfluorenone* (**53**) (978 mg, 95%), which crystallized from methanol as rectangular orange plates, m.p. 166—168 °C (Found: C, 68.85; H, 5.9%; M^+, 314. $C_{18}H_{18}O_5$ requires C, 68.8; H, 5.75%; *M*, 314); δ (300 MHz) 1.42 (6 H, d, Me_2 CH), 3.86 and 3.95 (each 3 H, s, OMe), 6.24 (1 H, s, D_2O-exchangeable OH), 7.05 (1 H, dd, $J_{6,7}$ 8.1, $J_{6,8}$ 1.1 Hz, 6-H), 7.11 (1 H, s, 1-H), 7.17 (1 H, dd, $J_{7,6}$ 8.1, $J_{7,8}$ 7.2 Hz, 7-H), and 7.25 (1 H, dd, $J_{8,7}$ 7.2, $J_{8,6}$ 1.1 Hz, 8-H).

3,5-*Dihydroxy*-2,4-*dimethoxy*-9H-*fluoren*-9-*one* (*Dengibsinin*) (**5**).—A solution of the foregoing fluorenone (**53**) (931 mg) in dichloromethane (15 ml) was stirred and cooled to −10 °C and a solution of boron trichloride (1.4 g) in dichloromethane (5 ml) was added. After 15 min the reaction was terminated by the addition of ethyl acetate and water. The crude product was isolated with ethyl acetate, and it crystallized from methanol as orange needles (660 mg, 82%) of *dengibsinin* (**5**), m.p. 225—227 °C (lit.,[1] 220 °C)* (Found: C, 66.5; H, 4.35. $C_{15}H_{12}O_5$ requires C, 66.15; H, 4.45%); *m/z* (35 eV) 273 (16%), 272 (M^+, 100), 258 (9), 257 (58), 239 (13), 227 (4), 214 (16), 211 (30), 199 (10), 183 (16), 158 (12), and 136 (13); δ (300 MHz) 3.95 and 4.14 (each 3 H, s, OMe), 6.19 (1 H, s, D_2O-exchangeable 3-OH), 6.98 (1 H, dd, $J_{6,7}$ 7.8, $J_{6,8}$ 1.5 Hz, 6-H), 7.09 (1 H, s, 1-H), 7.13 (1 H, dd, $J_{7,6}$ 7.8, $J_{7,8}$ 7.1 Hz, 7-H), 7.18 (1 H, dd, $J_{8,7}$ 7.1, $J_{8,6}$ 1.5 Hz, 8-H), and 9.15 (1 H, s, D_2O-exchangeable 5-OH); $\lambda_{max.}$ 272, 282, 307, 318, and 364 nm (ε 28 800, 30 500, 6 100, 6 000, and 6 200 respectively); $\lambda_{max.}$ (EtOH + NaOH) 262, 308, and 432 nm (ε 17 400, 24 200, and 10 700 respectively); $\nu_{max.}$(KBr) 3 280s, 1 692s, 1 605m, 1 595m, 1 582m, 1 479m, 1 451s, 1 430m, 1 385s, 1 310m, 1 278s, 1 255w, 1 220m, 1 195w, 1 160m, 1 130m, 1 082w, 1 060m, 1 037w, 990m, 938w, 905m, 878m, 852w, 789m, 768w, and 750m cm^{-1}; the *diacetate* (**54**) crystallized from methanol as yellow laths, m.p. 192—194 °C (lit.,[1] 180 °C)† (Found: C, 63.85; H, 4.45%; M^+, 356. $C_{19}H_{16}O_7$ requires C, 64.05; H, 4.55%; *M*, 356); δ (300 MHz) 2.36 and 2.38 (each 3 H, s, MeCO), 3.81 and 3.89 (each 3 H, s, OMe), 7.11 (1 H, dd, $J_{6,7}$ 8.1, $J_{6,8}$ 1.1 Hz, 6-H), 7.19 (1 H, s, 1-H), 7.27 (1 H, dd, $J_{7,6}$ 8.1, $J_{7,8}$ 7.2 Hz, 7-H), and 7.56 (1 H, dd, $J_{8,7}$ 7.2, $J_{8,6}$ 1.1 Hz, 8-H); $\lambda_{max.}$ 267, 306, 334, and 424 nm (ε 59 100, 3 100, 2 400, and 700 respectively).

Methyl 5-*Bromo*-2,3,4-*trimethoxybenzoate* (**56**).—A solution of bromine (6.23 g) in tetrachloromethane (35 ml) was added dropwise during 2.5 h to a solution of methyl 2,3,4-trimethoxybenzoate (**55**) (8.8 g)[14] in dichloromethane (75 ml). The solution was stirred for a further 1 h after the addition and the usual work-up gave the crude product as an oil which had undergone some partial demethylation as revealed by the ^1H n.m.r. spectrum. It was therefore methylated with iodomethane and potassium carbonate in DMF in the usual way. The *bromo compound* (**56**) was obtained as an oil (11.0 g, 93%), b.p. 180 °C at 1.0 mmHg (Kugelrohr) (Found: C, 43.6; H, 4.4; Br, 26.0%; M^+, 304/306. $C_{11}H_{13}BrO_5$ requires C, 43.3; H, 4.3; Br, 26.2%; *M*, 304/306); δ (80 MHz) 3.89, 3.91, 3.93, and 3.97 (each 3 H, s, OMe), and 7.77 (1-H, s, ArH).

Methyl 6-*Bromo*-2,3,4-*trimethoxybenzoate* (**63**).—A solution of sodium nitrite (1.5 g) in a little water was added dropwise to a stirred, ice-cooled suspension of methyl 6-amino-2,3,4-trimethoxybenzoate (**62**) (5.0 g)[15] in a mixture of conc. hydrobromic acid (50 ml) and ice (50 g). The solution was added at once to a solution of coppper(I) bromide (15 g) in conc. hydrobromic acid (25 ml) at 50 °C. After the addition the mixture was maintained at 50 °C for 15 min, diluted with ice–water, and extracted with ether. The crude product crystallized from dichloromethane–light petroleum as prisms (5.6 g, 89%) of the *bromo compound* (**63**), m.p. 87—88 °C (Found: C, 43.35; H, 4.35; Br, 26.3%; M^+, 304/306); δ (80 MHz) 3.83, 3.84, 3.90, and 3.91 (each 3 H, s, OMe), and 6.85 (1 H, s, ArH).

Methyl 5-*Bromo*-2-*hydroxy*-3,4-*dimethoxybenzoate* (**57**).—The bromo compound (**56**) (9.25 g) was dissolved in dichloromethane (75 ml) and the solution was cooled to 0 °C and stirred during the dropwise addition of a solution of boron trichloride (3.5 g) in dichloromethane (15 ml). The solution was stirred at 0 °C for 30 min and at room temperature for 30 min. The usual work-up gave the *bromo compound* (**57**) (8.6 g, 97%) as an oil, b.p. 175 °C at 0.5 mmHg (Kugelrohr), which eventually solidified, and which crystallized from light petroleum as needles, m.p. 54—55 °C (Found: C, 41.5; H, 3.8; Br, 27.5%; M^+, 290/292. $C_{10}H_{11}BrO_5$ requires C, 41.25; H, 3.8; Br, 27.45%; *M*, 290/292); δ (80 MHz) 3.92, 3.94, and 4.00 (each 3 H, s, OMe), 7.79 (1 H, s, ArH), and 10.90 (1 H, s, D_2O-exchangeable OH). On hydrolysis with aqueous methanolic sodium hydroxide in the usual way this compound afforded 5-*bromo*-2-*hydroxy*-3,4-*dimethoxybenzoic acid* (**58**) as needles (from ethyl acetate), m.p. 187—189 °C (Found: C, 39.25; H, 3.3; Br, 28.65. $C_9H_9BrO_5$ requires C, 39.0; H, 3.25; Br, 28.85%).

Attempted Decarboxylation of 5-*Bromo*-2-*hydroxy*-3,4-*dimethoxybenzoic Acid* (**58**).—The acid (**58**) (2.0 g), copper(I) oxide (80 mg), and 2,2′-bipyridyl (100 mg) were heated under gentle reflux under dry nitrogen in *N*,*N*-dimethylaniline (10 ml) during 1 h. The cooled mixture was poured into ice–dil. sulphuric acid and the crude product was isolated with ethyl acetate, chromatographed over silica gel with 5% ethyl acetate–light petroleum as eluant, and finally distilled under diminished pressure to yield 2,3-dimethoxyphenol (**59**) (861 mg, 78%) as an oil, b.p. 160 °C at 20 mmHg (Kugelrohr) (lit.,[18] 141.5—142.5 °C at 14 mmHg); *m/z* 154 (100%, M^+); δ (60 MHz; CCl_4) 3.64 and 3.68 (each 3 H, s, OMe), 5.72 (1 H, s, OH), and 6.04—6.72 (3 H, m, ArH).

2,3-*Dimethoxyphenol* (**59**).—2-Hydroxy-3,4-dimethoxybenzoic acid (25.2 g), blades from methanol, m.p. 172—174 °C (lit.,[16] 170 °C), copper(I) oxide (1.3 g), and 2,2′-bipyridyl (1.0 g) were heated under gentle reflux under dry nitrogen in *N*,*N*-dimethylaniline (135 ml) during 1 h. Work-up as described in the preceding experiment gave the phenol (**59**) as an oil (17.4 g, 89%), b.p. 160 °C at 20 mmHg (Kugelrohr), identical with that described above.

Bromination of 2,3-*Dimethoxyphenol* (**59**).—A solution of bromine (503 mg) in tetrachloromethane (10 ml) was added dropwise to a stirred solution of the substrate (**59**) (484 mg) in tetrachloromethane (5 ml) during 5 min. The usual work-up gave the product as an oil (720 mg, 98%) with the composition 90% 6-bromo-2,3-dimethoxyphenol (**60**); δ (60 MHz; CCl_4) *inter alia*, 6.19 and 6.93 (2 H, AB, *J* 9.0 Hz, ArH); and 10% 4-bromo-2,3-dimethoxyphenol (**61**); δ (60 MHz; CCl_4) *inter alia*, 6.46 and 6.96 (2 H, AB, *J* 9.0 Hz, ArH); as judged by integration of the ^1H n.m.r. spectrum. The ^1H n.m.r. spectrum of the major isomer was identical with that of authentic 6-bromo-2,3-dimethoxyphenol (**60**) (see below) recorded in CCl_4 at 60 MHz. The mixture migrated as one spot on silica gel on t.l.c. in a variety of solvent systems.

1-*Isopropoxy*-2,3-*dimethoxybenzene* (**64**).—Isopropylation of the phenol (**59**) in a manner similar to that described for compound (**6**) gave the *isopropyl ether* (**64**) (87%) as an oil, b.p. 145 °C at 15 mmHg (Found: C, 67.2; H, 8.3%; M^+, 196.

* Lit. m.p. for compound erroneously assigned structure (**2**).

† Lit. m.p. for compound erroneously assigned as 1,6-diacetoxy-5,7-dimethoxy-9*H*-fluoren-9-one.

$C_{11}H_{16}O_3$ requires C, 67.3; H, 8.2% *M*, 196); δ (80 MHz) 1.35 (6 H, d, Me_2CH), 3.85 (6 H, s, 2 × OMe), 4.53 (1 H, septet, $CHMe_2$), and 6.49—7.06 (3 H, m, ArH).

Bromination of 1-*Isopropoxy*-2,3-*dimethoxybenzene* (**64**).—A solution of bromine (5.03 g) in acetic acid (20 ml) was added dropwise to a stirred solution of the pyrogallol (**62**) (6.16 g) in acetic acid (50 ml) containing anhydrous sodium acetate (6.0 g). After the addition the mixture was poured into water and the acetic acid was neutralized by the addition of solid sodium carbonate. The crude product was isolated with ethyl acetate and subjected to radial chromatography with 2.5% ethyl acetate–light petroleum as developer; some mixed fractions were obtained. The first band, on elution, gave 1,5-*dibromo*-2-*isopropoxy*-3,4-*dimethoxybenzene* (464 mg, 4%) as an oil, b.p. 140 °C at 0.4 mmHg (Kugelrohr) (Found: C, 37.65; H, 3.95; Br, 44.95%; M^+, 352/354/356. $C_{11}H_{14}Br_2O_3$ requires C, 37.3; H, 4.0; Br, 45.15%; *M*, 352/354/356); δ (80 MHz) 1.34 (6 H, d, Me_2CH), 3.89 (3 H, s, OMe), 4.58 (1 H, septet, $CHMe_2$), and 7.49 (1 H, s, ArH).

The second band yielded 1-*bromo*-4-*isopropoxy*-2,3-*dimethoxybenzene* (**66**) (2.58 g, 30%) as an oil, b.p. 125 °C at 0.6 mmHg (Kugelrohr) (Found: C, 47.85; H, 5.35; Br, 29.0%; M^+, 274/276. $C_{11}H_{15}BrO_3$ requires C, 48.0; H, 5.5; Br, 29.05%; *M*, 274/276); δ (300 MHz) 1.36 (6 H, d, Me_2CH), 3.87 and 3.90 (each 3 H, s, OMe), 4.51 (1 H, septet, $CHMe_2$), and 6.59 and 7.17 (2 H, AB, *J* 9.0 Hz, ArH).

The final band supplied 1-*bromo*-2-*isopropoxy*-3,4-*dimethoxybenzene* (**65**) (2.68 g, 31%) as an oil, b.p. 125 °C at 0.6 mmHg (Kugelrohr) (Found: C, 48.2; H, 5.45; Br, 28.8%; M^+, 274/276); δ (300 MHz) 1.34 (6 H, d, Me_2CH), 3.846 and 3.848 (each 3 H, s, OMe), 4.62 (1 H, septet, CH), and 6.57 and 7.21 (2 H, AB, *J* 9.0 Hz, ArH).

Methyl 4-*Isopropoxy*-2,3-*dimethoxybenzoate* (**67**).—The Grignard reagent was prepared in the usual way, under dry argon, from 1-bromo-4-isopropoxy-2,3-dimethoxybenzene (**66**) (2.45 g), magnesium (250 mg), and anhydrous THF (18 ml). The mixture was poured onto an excess of solid carbon dioxide and after the carbon dioxide had disappeared the solution was diluted with hydrochloric acid and the crude product was extracted into ethyl acetate and purified by extraction with saturated aqueous sodium hydrogen carbonate. The crude acid, on work-up, was methylated with iodomethane and potassium carbonate in DMF at room temperature in the usual way. The *ester* (**67**) was obtained as an oil (1.35 g, 60%), b.p. 160 °C at 0.5 mmHg (Kugelrohr) (Found: C, 61.25; H, 7.25%; M^+, 254. $C_{13}H_{18}O_5$ requires C, 61.4; H, 7.15%; *M*, 254); δ (80 MHz) 1.39 (6 H, d, Me_2CH), 3.85, 3.88, and 3.93 (each 3 H, s, OMe), 4.70 (1 H, septet, $CHMe_2$), and 6.68 and 7.56 (2 H, AB, *J* 8.9 Hz, 5- and 6-H).

Reaction of Methyl 4-*Isopropoxy*-2,3-*dimethoxybenzoate* (**67**) *with Boron Trichloride*.—The ester (**67**) (1.14 g) was dissolved in anhydrous dichloromethane (10 ml) and the solution was stirred and cooled at −10 °C and treated with a solution of boron trichloride (800 mg) in dichloromethane (2.5 ml). Work-up after 15 min at −10 °C gave a crude product, which was purified by radial chromatography with 15% ethyl acetate–light petroleum as developer. The first band, on elution yielded *methyl* 2-*hydroxy*-4-*isopropoxy*-3-*methoxybenzoate* (**68**) (99 mg, 9%) as an oil, b.p. 140 °C at 0.5 mmHg (Kugelrohr) (Found: C, 59.85; H, 6.65%; M^+, 240. $C_{12}H_{16}O_5$ requires C, 60.0; H, 6.7%; *M*, 240); δ (80 MHz) 1.38 (6 H, d, Me_2CH), 3.87 and 3.91 (each 3 H, s, OMe), 4.65 (1 H, septet, $CHMe_2$), 6.46 and 7.54 (2 H, AB, *J* 9.0 Hz, 5-and 6-H), and 10.87 (1 H, s, D_2O-exchangeable OH). The second band afforded *methyl* 2,4-*dihydroxy*-3-*methoxybenzoate* (**69**) (631 mg, 71%) as an oil, b.p. 150 °C at 0.5 mmHg (Kugelrohr) (Found: C, 54.75; H, 5.1%; M^+, 198. $C_9H_{10}O_5$ requires C, 54.55; H, 5.1%; *M*, 198); δ (80 MHz) 3.91 and 3.97 (each 3 H, s, OMe), 6.34 (1 H, s, D_2O-exchangeable OH), 6.49 and 7.52 (2 H, AB, *J* 8.9 Hz, 5- and 6-H), and 11.10 (1 H, s, D_2O-exchangeable OH).

6-*Bromo*-2,3-*dimethoxyphenol* (**60**).—A solution of boron trichloride (950 mg) in dichloromethane (3 ml) was added at −10 °C to a stirred solution of 1-bromo-2-isopropoxy-3,4-dimethoxybenzene (**65**) (2.23 g) in dichloromethane (20 ml). After 15 min at −10 °C the usual work-up afforded the *phenol* (**60**) (1.54 g, 81%) as an oil, b.p. 125 °C at 0.3 mmHg (Kugelrohr) (Found: C, 41.05; H, 3.85; Br, 34.35%; M^+, 232/234. $C_8H_9BrO_3$ requires C, 41.25; H, 3.9; Br, 34.3%; *M*, 232/234); δ (80 MHz) 3.85 and 3.90 (each 3 H, s, OMe), 6.10 (1 H, s, D_2O-exchangeable OH), and 6.41 and 7.15 (2 H, AB, *J* 9.0 Hz, ArH).

2,5-*Di*-*isopropoxy*-3,4-*dimethoxy*-9H-*fluoren*-9-*one* (**72**) *and* 3,10-*Di*-*isopropoxy*-4-*methoxy*-6H-*dibenzo*[b,d]*pyran*-6-*one* (**71**).—The Grignard reagent was prepared in the usual way, under dry argon, from 1-bromo-4-isopropoxy-2,3-dimethoxybenzene (**66**) (6.7 g); it was allowed to react with the dihydrooxazole (**49**) (5.3 g) and the same sequence of reactions was applied to the product as that described in the synthesis of compounds (**39**) and (**40**). The crude product was chromatographed over silica gel with 10—30% ethyl acetate–light petroleum as eluant. The first band that was eluted afforded the *fluorenone* (**72**) (940 mg, 15%) as orange blades (from light petroleum), m.p. 72—73 °C (Found: C, 70.5; H, 6.75%; M^+, 356. $C_{21}H_{24}O_5$ requires C, 70.75; H, 6.8%; *M*, 356); δ (300 MHz) 1.39 and 1.43 (each 6 H, d, Me_2CH), 3.94 and 3.95 (each 3 H, s, OMe), 4.63 and 4.67 (each 1 H, septet, Me_2CH), 7.06 (1 H, dd, $J_{6,7}$ 7.0, $J_{6,8}$ 1.2 Hz, 6-H), 7.10 (1 H, s, 1-H), 7.16 (1 H, dd, $J_{7,8}$ 7.2, $J_{7,6}$ 7.0 Hz, 7-H), and 7.26 (1 H, dd, $J_{8,7}$ 7.2, $J_{8,6}$ 1.2 Hz, 8-H).

Further elution afforded the *dibenzopyran* (**71**) (2.37 g, 38%) as needles (from dichloromethane–light petroleum), m.p. 120—121 °C (Found: C, 70.4; H, 6.7%; M^+, 342. $C_{20}H_{22}O_5$ requires C, 70.15; H, 6.5%; *M*, 346); δ (300 MHz) 1.43 and 1.51 (each 6 H, d, Me_2CH), 3.98 (3 H, s, OMe), 4.70 and 4.80 (each 1 H, septet, $CHMe_2$), 6.89 (1 H, d, $J_{2,1}$ 9.4 Hz, 2-H), 7.30 (1 H, dd, $J_{9,8}$ 8.0, $J_{9,7}$ 1.3 Hz, 9-H), 7.42 (1 H, dd, $J_{8,9}$ 8.0, $J_{8,7}$ 7.9 Hz, 8-H), 8.03 (1 H, dd, $J_{7,8}$ 7.9, $J_{7,9}$ 1.3 Hz, 7-H), and 8.78 (1 H, d, $J_{1,2}$ 9.4 Hz, 1-H).

3-*Hydroxy*-2,5-*di*-*isopropoxy*-4-*methoxy*-9H-*fluoren*-9-*one* (**73**).—The foregoing fluorenone (**72**) (930 mg), piperidine (40 ml), and water (10 ml) were boiled and stirred under reflux under nitrogen for 40 h. The usual work-up afforded the crude product, which crystallized from light petroleum as scarlet needles (720 mg, 81%) of the *fluorenone* (**73**), m.p. 113—115 °C (Found: C, 70.05; H, 6.5%; M^+, 342. $C_{20}H_{22}O_5$ requires C, 70.15; H, 6.5%; *M*, 342); δ (300 MHz) 1.40 and 1.42 (each 6 H, d, Me_2CH), 3.86 (3 H, s, OMe), 4.64 and 4.66 (each 1 H, septet, Me_2CH), 6.20 (1 H, D_2O-exchangeable OH), 7.06 (1 H, dd, $J_{6,7}$ 7.1, $J_{6,8}$ 1.2 Hz, 6-H), 7.09 (1 H, s, 1-H), 7.17 (1 H, dd, $J_{7,8}$ 7.2, $J_{7,6}$ 7.1 Hz, 7-H), and 7.25 (1 H, dd, $J_{8,7}$ 7.2, $J_{8,6}$ 1.2 Hz, 8-H).

2,5-*Di*-*isopropoxy*-4-*methoxy*-3-(1-*phenyltetrazol*-5-*yloxy*)-9H-*fluoren*-9-*one* (**74**).—The foregoing hydroxyfluorenone (**73**) (262 mg), 5-chloro-1-phenyl-1*H*-tetrazole (152 mg), and potassium carbonate (300 mg) were stirred and heated at 90 °C (bath) in DMF (6 ml) under dry nitrogen for 22 h. The cooled suspension was diluted with water and extracted with ethyl acetate. The extract was washed successively with dil. aqueous ammonia until the aqueous phase was colourless, with water, and with saturated brine. The crude product crystallized from methanol as orange laths (322 mg, 87%) of the *tetrazole* (**74**),

m.p. 193—195 °C (Found: C, 66.4; H, 5.3; N, 11.35%; M^+, 486. $C_{27}H_{26}N_4O_5$ requires C, 66.65; H, 5.4; N, 11.5%; M, 486); δ (300 MHz) 1.16 and 1.40 (each 6 H, d, Me_2CH), 3.84 (3 H, s, OMe), 4.62 and 4.67 (each 1 H, septet Me_2CH), 7.14 (1 H, dd, $J_{6,7}$ 7.2, $J_{6,8}$ 1.1 Hz, 6-H), 7.16 (1 H, s, 1-H), 7.22 (1 H, dd, $J_{7,6}$ 7.2, $J_{7,8}$ 7.1 Hz, 7-H), 7.31 (1 H, dd, $J_{8,7}$ 7.1, $J_{8,6}$ 1.1 Hz, 8-H), 7.49—7.62 (3 H, m, *m*- and *p*-Ph), and 7.87—7.91 (2 H, m, *o*-Ph).

2,5-*Dihydroxy*-4-*methoxy*-9H-*fluoren*-9-*one* (*Dengibsin*) (**4**). —The tetrazole (**74**) (218 mg) and palladium–charcoal (Engelhard; 10%; 200 mg) were stirred together in benzene (24 ml), ethanol (10 ml), and water (7 ml), and hydrazine hydrate (98%; 2 ml) was added dropwise. After 1.5 h an additional amount of hydrazine hydrate (2 ml) was added and, after a further 1.5 h, palladium–charcoal (200 mg) and hydrazine hydrate (2 ml) were added. Two further additions of hydrazine hydrate (2 ml) were made at intervals of 1 h, and finally the reaction mixture was worked up after a further 1 h. The catalyst was separated by filtration and was washed with ethyl acetate. The filtrate and washings were washed in turn with water, dil. hydrochloric acid, and finally with saturated brine. The product was purified by radial chromatography with 15% ethyl acetate–light petroleum as developer and was obtained as an orange oil (95 mg, 65%). This material (**75**) was dissolved in dichloromethane (10 ml) and the solution was stirred, cooled to 0 °C, and treated with a solution of boron trichloride (650 mg) in dichloromethane (2 ml). After 15 min at room temperature the reaction mixture was worked up in the usual manner and the crude product was crystallized from methanol to give *dengibsin* (**4**) (56 mg, 79%) as rosettes of carmine needles, m.p. 238—240 °C (lit.,[1] 227 °C)* (Found: C, 69.5; H, 4.15. $C_{14}H_{10}O_4$ requires C, 69.4; H, 4.15%); *m/z* (35 eV) 243 (17%), 242 (M^+, 100), 227 (69), 199 (44), 171 (14), 155 (5), 142 (5), 126 (6), 121 (10), and 115 (17); δ (300 MHz; CD_3COCD_3) 4.13 (3 H, s, OMe), 6.78 (1 H, d, $J_{3,1}$ 2.0 Hz, 3-H), 6.81 (1 H, d, $J_{1,3}$ 2.0 Hz, 1-H), 6.95 (1 H, dd, $J_{6,7}$ 7.1, $J_{6,8}$ 2.1 Hz, 6-H), 7.09—7.17 (2 H, m, 7- and 8-H), and 8.94 (1 H, s, D_2O-exchangeable OH); $\lambda_{max.}$ 260, 274, 337, 474, and 486 nm (ε 36 800, 42 000, 4 000, 1 800, and 1 700 respectively); $\lambda_{max.}$ (EtOH + NaOH) 292, 402, and 562 nm (ε 43 400, 1 300, and 1 700 respectively); $\nu_{max.}$(KBr) 3 310s, 1 692s, 1 619m, 1 610m, 1 595m, 1 492s, 1 450m, 1 431m, 1 375m, 1 365m, 1 318s, 1 262s, 1 203m, 1 171w, 1 149m, 1 081w, 1 051w, 1 026m, 988w, 959m, 929m, 892w, 854m, 831w, 806m, 760m, 741m, 735m, and 720w cm^{-1}. The *diacetate* (**76**) formed yellow blades (from dichloromethane–light petroleum), m.p. 204—206 °C (lit.,[1] 193 °C)† (Found: C, 66.2; H, 4.3%; M^+, 326. $C_{18}H_{14}O_6$ requires C, 66.25; H, 4.3%; M, 326); δ (300 MHz) 2.32 and 2.37 (each 3 H, s, MeCO), 3.91 (3 H, s, OMe), 6.82 (1 H, d, $J_{3,1}$ 2.0 Hz, 3-H), 7.10 (1 H, dd, $J_{6,7}$ 7.2, $J_{6,8}$ 1.1 Hz, 6-H), 7.12 (1 H, d, $J_{1,3}$ 2.0 Hz, 1-H), 7.28 (1 H, dd, $J_{7,8}$ 7.3, $J_{7,6}$ 7.2 Hz, 7-H), and 7.59 (1 H, dd, $J_{8,7}$ 7.3, $J_{8,6}$ 1.1 Hz, 8-H); $\lambda_{max.}$ 257, 265, 320, and 418 nm (ε 30 800, 31 500, 3 000, and 1 200 respectively).

* Lit. m.p. for compound erroneously assigned structure (**1**).

† Lit. m.p. for compound erroneously assigned as 1,5-diacetoxy-7-methoxy-9*H*-fluoren-9-one.

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