Naturally Occurring Dibenzofurans. Part 3.[1] On the Structures of the Rhodomyrtoxins

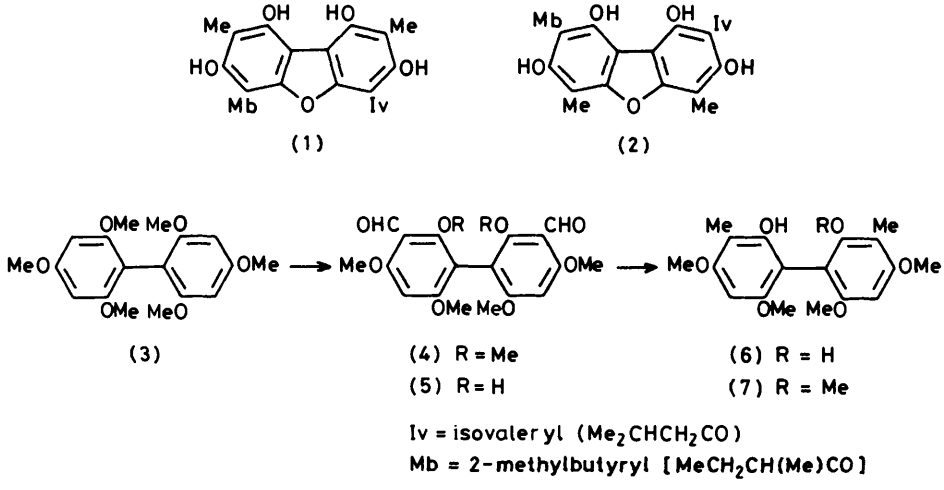
Melvyn V. Sargent * and Peter O. Stransky
Department of Organic Chemistry, University of Western Australia, Nedlands, Western Australia, 6009, Australia
Vincent A. Patrick and Allan H. White
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia, 6009, Australia

The degradation product of rhodomyrtoxin and ψ-rhodomyrtoxin, metabolites of the fruit of *Rhodomyrtus macrocarpa* Benth., previously assigned the structure 1,3,7,9-tetramethoxy-2,8-dimethyldibenzofuran (13) is now shown to be 1,3,7,9-tetramethoxy-4,6-dimethyldibenzofuran (15), the structure of this compound being determined by *X*-ray diffraction. By the synthesis of 1,1'-(1,3,7,9-tetrahydroxy-2,6-dimethyldibenzofuran-4,8-diyl)-3,3'-dimethyldibutan-1-one (17) and 1,1'-(1,3,7,9-tetrahydroxy-4,6-dimethyldibenzofuran-2,8-diyl)-2,3'-dimethyldibutan-1-one (2), structure (18), 1,1'-(1,3,7,9-tetrahydroxy-2,8-dimethyldibenzofuran-4,6-diyl)-3,3'-dimethyldibutan-1-one (18), is proposed for rhodomyrtoxin, and structure (1), 1,1'-(1,3,7,9-tetrahydroxy-2,8-dimethyldibenzofuran-4,6-diyl)-2,3'-dimethyldibutan-1-one (1), is confirmed for ψ-rhodomyrtoxin.

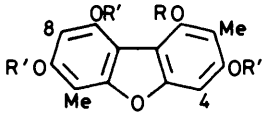
The constituents of the fruits of *Rhodomyrtus macrocarpa* Benth., the Australian finger cherry, have attracted the attention of organic chemists since it has been reported that their consumption can lead to blindness. Trippett [2] first examined this problem and isolated rhodomyrtoxin to which he assigned the partial structure of a di-isovaleryldimethyldibenzofurantetraol after extensive degradative work. Treatment of rhodomyrtoxin with boiling hydriodic acid produced a dimethyldibenzofurantetraol which on reisovalerylation with isovaleric acid and boron trifluoride provided not rhodomyrtoxin but an isomer, isorhodomyrtoxin. A rearrangement must therefore have occurred during the degradation of rhodomyrtoxin since rhodomyrtoxin was stable under the conditions of the isovalerylation reaction.

Ollis and his co-workers [3] examined the problem afresh but were unable to isolate rhodomyrtoxin and instead obtained yet another isomer, ψ-rhodomyrtoxin, to which they assigned the structure (1). Degradation of ψ-rhodomyrtoxin under acidic or basic reaction conditions afforded isovaleric and 2-methylbutyric acids and a dimethyldibenzofurantetraol characterised as its tetra-*O*-methyl ether, the symmetry of which was indicated by its ^{1}H n.m.r. spectrum as shown by the equivalence of the aromatic protons, the aromatic methyl groups, and two pairs of methoxy-groups. This compound was identical with that obtained by Trippett by degradation of rhodomyrtoxin. It was argued that no rearrangement would occur during the degradation of ψ-rhodomyrtoxin under basic conditions so that an assignment of the constitution of the degradation product would lead to the structure of ψ-rhodomyrtoxin.

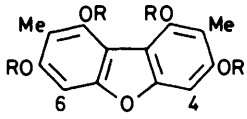
Synthetic evidence on this point was sought by Ollis and his co-workers. The synthesis of the tetra-*O*-methyl ether of the degradation product started from the known [4] hexamethoxybiphenyl (3) (Scheme 1) which on Vilsmeier-Haack formylation provided the dialdehyde (4). This was selectively demethylated with hydrobromic acid thus affording the biphenyldiol (5) and thence by Clemmensen reduction the dimethyl compound (6). Ring-closure of compound (6) was achieved with hot phosphoric acid and gave a dibenzofuranol, assigned structure (8) because of its mode of formation and since on methylation it gave the unsymmetrical dibenzofuran (9). However by subjecting the methyl ether (7) of compound (6) to the same conditions followed by methylation the Ollis group were able to secure, in poor yield, a symmetrical



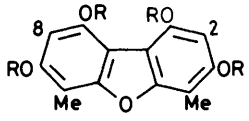
Scheme 1



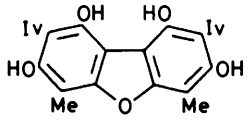
(8) R=H, R'=Me
(9) R=R'=Me
(10) R=R'=H
(11) R=Ac, R'=Me



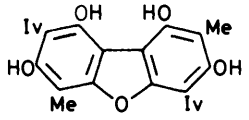
(12) R=H
(13) R=Me



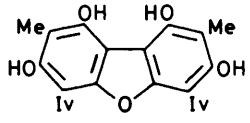
(14) R=H
(15) R=Me



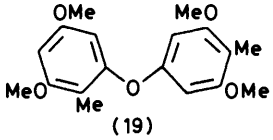
(16)



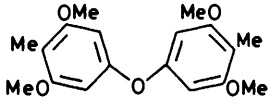
(17)



(18)



(19)



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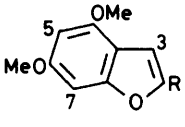


(21) R=H
(22) R=CO_2Et

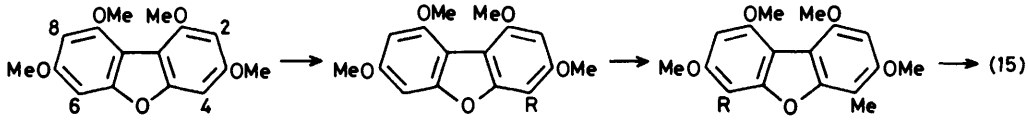
Iv = isovaleryl (Me_2CHCH_2CO)

dibenzofuran identical with the tetra-*O*-methyl ether of the degradation product. This synthesis is structurally ambiguous. By an argument based on the chemical shifts of the hydroxy-protons in the ^1H n.m.r. spectrum of ψ-rhodomyrtoxin a distinction was made between the possible structures (1), an *o*-hydroxy-carbonyl situation, and (2), an *o*,*o*-dihydroxy-carbonyl situation, for ψ-rhodomyrtoxin. Structure (1) was proposed. If this argument is correct the degradation product must have structure (12) and was assumed to be thermodynamically more stable than its isomers (10) and (14). Structure (13) is therefore that of the tetra-*O*-methyl ether of the degradation product and either structure (16) or (17) follows for rhodomyrtoxin. Isorhodomyrtoxin must therefore have constitution (18).

The ^1H n.m.r. spectrum of the unsymmetrical dibenzofuran (9) exhibited singlets for the aromatic protons at δ 6.84 and 6.43 assigned by Ollis and his co-workers to the 4- and 8-protons. The symmetrical dibenzofuran obtained by degradation and by synthesis and assigned structure (13) exhibited a single aromatic proton resonance at δ 6.37 assigned to the 4- and 6-protons. If the aromatic proton assignments for compound (9) are correct then this value is more in keeping with that expected for the 2- and 8-protons of compound (15), and thus the degradation product should be assigned structure (14). It also appeared more likely to us that the dimethyldibenzofurantetraol (14) would be thermodynamically more stable than the alternative symmetrical isomer (12) since the methyl groups in the former compound are removed from proximity to the hindered 1- and 9-positions.

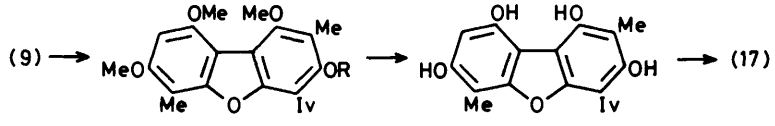
We therefore sought to verify the ^1H n.m.r. spectral assignments for the unsymmetrical dibenzofuran (9), which we had previously synthesized unambiguously by ring-closure of the diphenyl ether (19) by palladium(II) acetate.[5] For this purpose we repeated the synthesis of Ollis and his co-workers. A number of improvements in this synthesis, notably the use of boron trichloride in the partial demethylation step, are recorded in the Experimental section. The acetate (11) of the dibenzofuranol (8) was prepared and its ^1H n.m.r. spectrum was compared with that of the dibenzofuranol. The chemical shift of the 4-proton in the acetate (11) was 0.36 p.p.m. further downfield than the similar proton in the dibenzofuranol (8). The value of this shift is typical for a proton in the *para*-position to a phenolic hydroxy-group [6] so that the assignments for the aromatic proton signals of the dibenzofuranol (9) are confirmed.

We next attempted the synthesis of the symmetrical dibenzofuran (13) by ring-closure of the diphenyl ether (20) with palladium(II) acetate but this reaction failed under various conditions. It was therefore decided to seek more concrete evidence for the structure of the degradation product assigned structure (13) by Ollis and his co-workers, but for which we preferred structure (15). We expected that prolonged treatment of the biphenyldiol (6) with boiling hydrobromic acid in acetic acid followed by methylation of the product would



(23) (24) R = CHO (25) R = CH_2OH (26) R = Me (27) R = CHO (28) R = CH_2OH

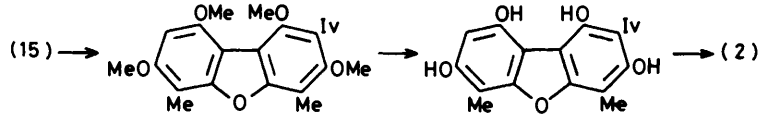
Scheme 2



(29) R = Me (30) R = H (31)

Iv = isovoleryl (Me_2CHCH_2CO)

Scheme 3



(32) (33)

Iv = isovaleryl (Me_2CHCH_2CO)

Scheme 4

provide the tetra-*O*-methyl ether of the thermodynamically most stable of the three possible dibenzofurans. This proved to be the case and an additional product was the unsymmetrical dibenzofuran (9). Similarly treatment of the latter compound with boiling hydriodic acid followed by methylation afforded the same symmetrical dibenzofuran. We also synthesized this compound by a less ambiguous method. The known [4] tetramethoxydibenzofuran (23) (Scheme 2) was readily obtained by treatment of the hexamethoxybiphenyl (3) with boiling hydriodic acid followed by methylation. Foster and Robertson [7] showed that the 4,6-dimethoxybenzofurans (21) and (22) underwent Gattermann formylation at the 7-position. We therefore reasoned that the tetramethoxydibenzofuran (23) would undergo formylation at the 4-position. Vilsmeier-Haack formylation of compound (23) smoothly furnished the monoaldehyde (24) which was reduced initially to the hydroxymethyl compound (25) with lithium aluminium hydride, and this in turn afforded the methyl compound (26) on catalytic reduction. As expected from this structural assignment compound (26) exhibited the 2-proton as a singlet at δ 6.44 in its ^1H n.m.r. spectrum. Formylation of compound (26) gave the aldehyde (27) which was converted, *via* the alcohol (28), into a symmetrical tetramethoxydimethyldibenzofuran. This compound was identical with that obtained by us both by ring closure of the biphenyldiol (6) and by rearrangement of the unsymmetrical dibenzofuran (9). Absolute proof of its structure as (15) was obtained by the *X*-ray method. There is little doubt that this is the same compound as that obtained by Ollis and his co-workers and assigned structure (13) since the ^1H n.m.r. spectra of the two are identical although we observed a slightly lower m.p.

Given that no rearrangement occurred during the degradation of ψ-rhodomyrtoxin by base and since ψ-rhodomyrtoxin exhibits a high degree of symmetry as shown by its ^1H n.m.r. spectrum and those of its derivatives, then the above evidence requires the revision of the structure of ψ-rhodomyrtoxin to (2). Similarly only structures (17) and (18) are now tenable for rhodomyrtoxin, and isorhodomyrtoxin must be (16). We now embarked on the synthesis of compounds (17) and (2).

For the synthesis of the former compound the starting material was the unsymmetrical dibenzofuran (9) (Scheme 3). This was acylated with isovaleryl chloride and tin(IV) chloride at 0—25 °C and afforded a mixture of the monoisovaleryl compound (29) and the product of its selective demethylation (30). Extending the reaction time increased the extent of selective demethylation. Such demethylations have been observed before under similarly mild conditions.[8] Methylation of compound (30) gave the methyl ether (29). The isovaleryl group had entered the 4-position in compound (9) since the lone aromatic proton in compound (29) resonated at δ 6.44 in its ^1H n.m.r. spectrum. An attempt to introduce a second isovaleryl group into compound (29) by the above method failed so that compound (29) was demethylated with boron tribromide whereupon it afforded the tetraol (31). This was isovalerylated with isovaleric acid and boron trifluoride–diethyl ether and gave compound (17). The physical data for this compound, m.p. 209—211 °C, and its tetra-acetate, a viscous oil, were different from those recorded by Trippett [2] for rhodomyrtoxin, m.p. 198—199 °C, and its tetra-acetate, m.p. 191—192 °C, although a direct comparison was not possible. Rhodomyrtoxin must therefore have structure (18).

Isovalerylation of the symmetrical dibenzofuran (15) (Scheme 4) with isovaleryl chloride and tin(IV) chloride again occurred with partial demethylation but methylation of the crude product afforded the isovaleryl compound (32) different from its isomer (29). Demethylation of the crude isovaleryl-

ation product with boron tribromide gave the tetraol (33); again this was different from its isomer (31) thus providing evidence that no rearrangement had occurred. The tetraol (33) exhibited a very low field intramolecularly H-bonded hydroxy-proton signal in its ^{1}H n.m.r. spectrum which casts doubt on the validity of the n.m.r. spectroscopic argument used by the Ollis group to establish structure (1) for ψ-rhodomyrtoxin.

Treatment of the tetraol (33) with 2-methylbutyric acid and boron trifluoride–diethyl ether supplied compound (2). Although this compound had a m.p. identical with that of ψ-rhodomyrtoxin and a similar ^{1}H n.m.r. spectrum the synthetic tetra-acetate melted 76 °C higher than that recorded for the tetra-acetate of ψ-rhodomyrtoxin. We are therefore forced to the conclusion that structural assignment (1), by Ollis and his co-workers, for ψ-rhodomyrtoxin is fortuitously correct in spite of the wrong assignment of the structure of the degradation product. This conclusion suggested that a rearrangement should have occurred during the degradation of ψ-rhodomyrtoxin under basic conditions. We therefore subjected the synthetic compound (31) to the same degradation conditions and then methylated the crude product and examined this by g.l.c.–m.s. We obtained only compound (29) and no degradation products could be detected. Similarly only hydrolysis of the ester groups and no degradation occurred when the tetra-acetate of the di-isovaleryl compound (17) was subjected to the same treatment.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus. Light petroleum was the fraction b.p. 58—65 °C. All organic extracts were dried over sodium sulphate prior to evaporation. Silica gel was B.D.H. 60—120 mesh and alumina was Fluka neutral, activity I (Brockmann). Crude products were pre-adsorbed from dichloromethane solution prior to chromatography. Preparative t.l.c. plates (20 × 20 × 0.1 cm) were coated with Merck Kieselgel GF_{254}. N.m.r. spectra were determined at 60 MHz using a Hitachi-Perkin-Elmer R-24B, at 80 MHz using a Brüker WP-80, or at 90 MHz using a Brüker HX-90 instrument. Mass spectra were recorded with a Hewlett-Packard 5896 (low resolution) or a Varian MAT 311 (high resolution) instrument both operating at 70 eV. Hydriodic acid (*d* 1.7) before use was heated to boiling and clarified by the dropwise addition of 50% phosphinous acid.

1-*Iodo*-2,4,6-*trimethoxybenzene*.—Iodine (12.7 g) in chloroform (200 ml) was added in drops during 0.5 h to a stirred solution of 1,3,5-trimethoxybenzene (8.4 g) and silver trifluoroacetate (11.05 g) in chloroform (100 ml). The suspension was stirred for a further 10 min and the precipitated silver iodide was separated by filtration and washed with a little chloroform. The filtrate was washed in turn with aqueous sodium thiosulphate, water, and finally with saturated brine. The crude product formed prisms (13.0 g), m.p. 121—122 °C (lit.,[4] 119—121 °C) (from dichloromethane–light petroleum); δ ($CDCl_3$, 60 MHz) 3.77 (3 H, s, OMe), 3.79 (6 H, s, 2 × OMe), and 6.03 (2 H, s, 2 × ArH).

2,2′,4,4′,6,6′-*Hexamethoxy*-1,1′-*biphenyl* (3).—This was prepared in 75% yield by Ullmann reaction [3] under dry nitrogen between the foregoing iodo-compound and copper bronze activated by the method of Vogel [9] and dried at 30 °C and 0.01 mmHg for 12 h. It formed rods from chloroform–methanol (charcoal), m.p. 155 °C (lit.,[3] 155 °C); δ ($CDCl_3$, 60 MHz) 3.62 (12 H, s, 4 × OMe), 3.74 (6 H, s, 2 × OMe), and 6.11 (4 H, s, 4 × ArH).

2,2′,4,4′,6,6′-*Hexamethoxy*-1,1′-*biphenyl*-3,3′-*dicarbaldehyde* (4).—Phosphoryl chloride (5 ml) was added in drops to a stirred suspension of the biphenyl (3) (5.0 g) in dry *NN*-dimethylformamide (20 ml) at 0 °C. After the addition the mixture was heated on a steam-bath for 2.75 h. The cooled mixture was diluted with ice and water and stirred for 19 h. The product was separated by filtration, dried *in vacuo*, and crystallized from dichloromethane–light petroleum whereupon it formed rods of the dialdehyde (4) (4.85 g), m.p. 220—221 °C (lit.,[3] 221 °C); δ ($CDCl_3$, 60 MHz) 3.49, 3.74, and 3.88 (each 6 H, s, 2 × OMe), 6.23 (2 H, s, 2 × ArH), and 10.14 (2 H, s, 2 × CHO).

2,2′-*Dihydroxy*-4,4′,6,6′-*tetramethoxy*-1,1′-*biphenyl*-3,3′-*dicarbaldehyde* (5).—Boron trichloride (52.5 g) was dissolved in dry dichloromethane (250 ml) at −10 °C and the solution was stirred during the addition in drops of a solution of the aldehyde (4) (10.4 g) in dichloromethane. After the mixture had been stirred for 10 min at −10 °C a precipitate formed and after 50 min the suspension was poured with caution into a large volume of ice and water. The organic phase was extracted with ethyl acetate in the usual way. The crude product crystallized from ethyl acetate as clusters of prisms (9.6 g), m.p. 257—258 °C (lit.,[3] 257 °C).

4,4′,6,6′-*Tetramethoxy*-3,3′-*dimethyl*-1,1′-*biphenyl*-2,2′-*diol* (6).—The dialdehyde (5) (9.6 g), zinc amalgam [from zinc dust (100 g)], water (160 ml), glacial acetic acid (250 ml), and concentrated hydrochloric acid (160 ml) were stirred and heated under reflux for 2 h. The mixture was rapidly filtered through Celite and the pad was washed with ethyl acetate. The cooled filtrate was diluted with more ethyl acetate and washed successively with water, saturated aqueous sodium hydrogen carbonate, water, and finally with saturated brine. The crude product formed plates (8.25 g) of the diol (6) (from dichloromethane–light petroleum), m.p. 203—204 °C (lit.,[3] 205 °C); δ ($CDCl_3$, 60 MHz) 2.03 (6 H, s, 2 × Me), 6.38 and 6.23 (each 6 H, s, 2 × OMe), 4.94 (2 H, s, 2 × OH), and 6.03 (2 H, s, 2 × ArH).

3,7,9-*Trimethoxy*-2,6-*dimethyldibenzofuran*-1-*ol* (8).—The powdered biphenyldiol (6) (4.0 g) was added in portions to stirred orthophosphoric acid (400 ml) at 120 °C during 5 min. The mixture was stirred at this temperature for 1.5 h longer and then poured on ice. The crude product obtained by extraction with ethyl acetate was chromatographed over silica gel with 5—10% ethyl acetate–light petroleum as eluant. The dibenzofuranol (8) (1.6 g) crystallized from dichloromethane–light petroleum (charcoal) as laths, m.p. 175—176 °C (lit.,[3] 175 °C); δ ($CDCl_3$, 90 MHz) 2.18 and 2.27 (each 3 H, s, Me), 3.81, 3.84, and 3.96 (each 3 H, s, OMe), 6.25 (1 H, s, 8-H), 6.58 (1 H, s, 4-H), and 8.44 (1 H, s, D_2O exchangeable OH); *m/z* 303 (16.1%), 302 (93.1, M^+), 288 (18.2), 287 (100), 257 (15.3), 229 (11.6), 151 (38.8), 136 (10.8), and 128 (10.6). Acetylation in the usual way with pyridine and acetic anhydride (steam-bath) gave the *acetate* (11) as needles (from dichloromethane–light petroleum), m.p. 203—204 °C (Found: C, 66.3; H, 5.9. $C_{19}H_{20}O_6$ requires C, 66.25; H, 5.85%); δ ($CDCl_3$, 90 MHz) 2.13 and 2.31 (each 3 H, s, Me), 2.41 (3 H, s, MeCO), 3.86 (6 H, s, 2 × OMe), 3.92 (3 H, s, OMe), 6.35 (1 H, s, 8-H), and 6.94 (1 H, s, 4-H); *m/z* 345 (11.5%), 344 (53.4, M^+), 302 (100), 287 (87.4), and 272 (12.9).

Di-(3,5-*dimethoxy*-4-*methylphenyl*) *Ether* (20).—3,5-Dimethoxy-4-methylphenol [10] (740 mg), methyl 6-bromo-2,4-dimethoxy-3-methylbenzoate [11] (1.32 g), and dry finely divided potassium carbonate (1.32 g) in anhydrous pyridine (15 ml) were stirred and heated under dry nitrogen at 130 °C

(bath) and copper(II) oxide [12] (600 mg) was then added. The mixture was then stirred and heated under reflux for 18 h. The cooled mixture was diluted with ether and filtered through Kieselguhr. The filtrate was washed in turn with dilute hydrochloric acid, dilute sodium hydroxide, water, and finally saturated brine. Chromatography of the crude product over silica gel with 2.5% ethyl acetate–light petroleum as eluant gave methyl 4,6-dimethoxy-2-(3,5-dimethoxy-4-methylphenoxy)-5-methylbenzoate (668 mg) as an oil. This and potassium hydroxide (1.0 g) in dimethyl sulphoxide (20 ml) and water (5 ml) were heated on a steam-bath for 4 h. The crude acid, obtained in the usual way, was stirred and heated with copper chromite (500 mg) in anhydrous quinoline (25 ml) at 200 °C (bath) under dry nitrogen for 4 h. The usual work-up gave the *diphenyl ether* (20) (356 mg) as prisms (from ether–pentane), m.p. 133—135 °C (Found: C, 67.8; H, 6.9%; M^+, 318. $C_{18}H_{20}O_5$ requires C, 67.9; H, 6.95%; *M*, 318); δ ($CDCl_3$, 80 MHz) 2.00 (6 H, s, 2 × Me), 3.66 (12 H, s, 4 × OMe), and 6.15 (4 H, s, 4 × ArH).

Ring-closure of 4,4',6,6'-*Tetramethoxy*-3,3'-*dimethyl*-1,1'-*biphenyl*-2,2'-*diol* (6) *under Conditions of Thermodynamic Control.*—The diol (6) (610 mg), 48% hydrobromic acid (12 ml), and glacial acetic acid (12 ml) were stirred and heated under reflux under dry nitrogen for 18 h when examination by t.l.c. (silica gel; benzene–dioxan–acetic acid, 36 : 9 : 1) showed only two mobile spots. The solution was cooled and diluted with water. Extraction with chloroform removed only acetic acid (t.l.c.) and the crude products were extracted with ethyl acetate. The extract was washed in turn with water, sodium pyrosulphite solution, water, and finally saturated brine. The crude products were stirred with anhydrous potassium carbonate (3.0 g) and iodomethane (2 ml) in dry *NN*-dimethylformamide (15 ml) for 24 h under dry nitrogen. The usual work-up gave a crude product which was chromatographed over alumina with 10% ethyl acetate–light petroleum as eluant. Early fractions gave 1,3,7,9-tetramethoxy-2,6-dimethyldibenzofuran (9) (115 mg) as needles (from light petroleum), m.p. 114—115 °C (lit.,[3] 116 °C). It was identical by the usual criteria with an authentic sample [5] and with material prepared by methylation of 3,7,9-trimethoxy-2,6-dimethyldibenzofuran-1-ol (8), δ ($CDCl_3$, 90 MHz) 2.25 and 2.33 (each 3 H, s, Me), 3.84 (6 H, s, 2 × OMe), 3.88 and 4.00 (each 3 H, s, OMe), and 6.41 and 6.84 (each 1 H, s, 8- and 4-H); *m/z* 317 (16.5%), 316 (100, M^+), 302 (11.1), 301 (41.6), 286 (13.6), 271 (12.1), 258 (14.5), 158 (24.7), 143 (10.0), 128 (12.2), and 115 (10.0). Further elution gave 1,3,7,9-*tetramethoxy*-4,6-*dimethyldibenzofuran* (15) (215 mg) which formed prisms from ethyl acetate–light petroleum or ethanol, m.p. 192—193 °C (lit.,[2,3] 203—204 °C, 204 °C) not raised after several recrystallizations (Found: C, 68.6; H, 6.5%. $C_{18}H_{20}O_5$ requires C,68.35; H, 6.35%); δ ($CDCl_3$, 90 MHz) 2.34 (6 H, s, 2 × Me), 3.88 and 3.98 (each 6 H, s, 2 × OMe), and 6.41 (2 H, s, 2- and 8-H); *m/z* 317 (18.2%), 316 (100, M^+), 302 (19.9), 301 (75.5), 258 (16.5), 257 (12.1), 243 (13.3), 242 (13.5), 158 (36.7), 128 (18.0), and 115 (17.5).

Rearrangement of 1,3,7,9-*Tetramethoxy*-2,6-*dimethyldibenzofuran* (9).—The dibenzofuran (9) (100 mg) was heated under reflux under dry nitrogen in hydriodic acid (5 ml) for 2 h. The cooled mixture was diluted with water and extracted with ethyl acetate. The extract was washed in turn with saturated sodium hydrogen carbonate solution, sodium pyrosulphite solution, water, and finally with saturated brine. The crude product was methylated as described above and the crude product was subjected to preparative t.l.c. (35% ethyl acetate–light petroleum). Extraction of the major mobile band gave 1,3,7,9-tetramethoxy-4,6-dimethyldibenzofuran (15) (24 mg) as prisms (from light petroleum), m.p. and mixed m.p. 192—193 °C.

1,3,7,9-*Tetramethoxydibenzofuran* (23).—The biphenyl (3) (5.0 g) was heated under reflux under dry nitrogen for 0.5 h with hydriodic acid (50 ml). The cooled reaction mixture was diluted with water and extracted with ethyl acetate. The extract was washed successively with water, sodium pyrosulphite solution, water, and finally with saturated brine. The crude product was methylated as described above and the product was chromatographed over alumina with 20% dichloromethane–light petroleum as eluant. The dibenzofuran (23) (1.6 g) formed needles (from methanol), m.p. 112—113 °C not raised after several recrystallizations (lit.,[4] 118—119 °C); δ ($CDCl_3$, 90 MHz) 3.84 and 3.96 (each 6 H, s, 2 × OMe) and 6.40 and 6.65 (4 H, AB, *J* 2.0 Hz, 2-, 8-H and 4-, 6-H).

1,3,7,9-*Tetramethoxydibenzofuran*-4-*carbaldehyde* (24).—The dibenzofuran (23) (2.0 g) in dry *NN*-dimethylformamide (17 ml) was stirred and cooled to 0 °C and phosphoryl chloride (8 ml) was added in drops over 15 min. The mixture was stirred at room temperature for 1 h and then ice and water were added to the thick paste followed by sodium acetate (8 g). After 3 h the suspension was extracted with ethyl acetate in the usual way. The *aldehyde* (24) (2.0 g) formed glistening plates (from methanol), m.p. 177—178 °C (Found: C, 64.15; H, 5.2. $C_{17}H_{16}O_6$ requires C, 64.55; H, 5.1%); δ ($CDCl_3$, 90 MHz) 3.83, 3.89, 3.90, and 3.97 (each 3 H, s, OMe), 6.18 (1 H, s, 2-H), 6.36 and 6.81 (2 H, AB, *J* 2.0 Hz, 8- and 6-H), and 10.41 (1 H, s, CHO); *m/z* 317 (17.8), 316 (100, M^+), and 301 (28.7).

1,3,7,9-*Tetramethoxydibenzofuran*-4-*ylmethanol* (25).—The aldehyde (24) (1.9 g) in anhydrous tetrahydrofuran (150 ml) was added in drops with stirring to lithium aluminium hydride (800 mg) in anhydrous tetrahydrofuran (100 ml). The mixture was stirred and heated under reflux for 0.5 h and then cooled in ice and stirred and treated with an excess of saturated sodium sulphate solution until coagulation occurred. The organic phase was decanted and the magma remaining was extracted with hot ethyl acetate. The *alcohol* (25) (1.7 g) formed rods (from ethyl acetate–light petroleum), m.p. 153—154 °C (Found: C, 64.1; H, 5.75. $C_{17}H_{18}O_6$ requires C, 64.15; H, 5.7%); δ ($CDCl_3$, 80 MHz) 2.30 (1 H, t, *J* 5.7 Hz, OH), 3.86, 3.93, 3.98, and 4.01 (each 3 H, s OMe) 4.97 (2 H, d, *J* 5.7 Hz, CH_2), 6.40 and 6.70 (2 H, AB, *J* 1.7 Hz, 8- and 6-H), and 6.41 (1 H, s, 2-H); *m/z* 319 (16.5%), 318 (100, M^+), 303 (19.7), 302 (7.8), 301 (10.7), 244 (21.4), 159 (20.9), and 151 (11.7).

1,3,7,9-*Tetramethoxy*-4-*methyldibenzofuran* (26).—The alcohol (25) (400 mg) and 10% palladized charcoal (250 mg, Engelhard) were stirred under hydrogen in ethyl acetate (40 ml) until absorption ceased (3 h). The usual work-up gave the *dibenzofuran* (26) (375 mg) as prisms (from light petroleum), m.p. 110—111 °C (Found: C, 66.95; H, 6.15. $C_{17}H_{18}O_5$ requires C, 67.55; H, 6.0%); δ ($CDCl_3$, 80 MHz) 2.34 (3 H, s, Me), 3.88, 3.91, 3.96, and 4.00 (each 3 H, s, OMe), 6.40 and 6.72 (2 H, AB, *J* 2.3 Hz, 8- and 6-H), and 6.44 (1 H, s, 2-H); *m/z* 303 (18.3%), 302 (100, M^+), 288 (15.8), 287 (84.7), 244 (20.1), 243 (14.2), 229 (13.3), 227 (12.4), 151 (24.6), and 115 (13.5).

1,3,7,9-*Tetramethoxy*-6-*methyldibenzofuran*-4-*carbaldehyde* (27).—Formylation of the methyldibenzofuran (26) in the manner described for compound (23) gave the *aldehyde* (27) (97%) as prisms (from ethyl acetate), m.p. 241—244 °C (decomp.) (Found: C, 65.5; H, 5.8. $C_{18}H_{18}O_6$ requires C, 65.45; H, 5.5%); δ (CD_3SOCD_3, 80 MHz) 2.26 (3 H, s, Me),

3.91, 3.93, 4.02, and 4.06 (each 3 H, s, OMe), 6.62 and 6.64 (each 1 H, s, ArH), and 10.37 (1 H, s, CHO); *m/z* 331 (16.9%), 330 (100, M^+), 315 (48.9), 244 (11.3), 127 (10.6), and 115 (14.4).

1,3,7,9-*Tetramethoxy*-6-*methyldibenzofuran*-4-*ylmethanol* (28).—Reduction of the aldehyde (27) in the manner described for compound (24) gave the alcohol (28) (83%) as prisms (from ethyl acetate), m.p. 192—193 °C (Found: C, 64.85; H, 6.15. $C_{18}H_{20}O_6$ requires C, 65.05; H, 6.15%); δ ($CDCl_3$, 80 MHz) 1.67 (1 H, s, OH), 2.32 (3 H, s, Me), 3.90, 3.92, 3.98, and 4.00 (each 3 H, s, OMe), 4.99 (2 H, s, CH_2), and 6.38 and 6.42 (each 1 H, s, ArH); *m/z* 333 (19.1%), 332 (100, M^+), 317 (36.1), 259 (12.5), 258 (18.1), 244 (14.7), 243 (10.8), 228 (10.0), 166 (24.7), 158 (13.5), 135 (12.6), 128 (15.1), 127 (12.2), and 115 (11.1).

1,3,7,9-*Tetramethoxy*-4,6-*dimethyldibenzofuran* (15).—Reduction of the alcohol (28) in the manner described for compound (25) gave the dimethyldibenzofuran (15) (95%) as prisms (from ethanol), m.p. and mixed m.p. 192—193 °C.

Isovalerylation of 1,3,7,9-*Tetramethoxy*-2,6-*dimethyldibenzofuran* (9).—(*a*) Tin(IV) chloride (0.2 ml) in dry dichloromethane (3 ml) was added in drops to a stirred solution of the substrate (9) (111 mg) and isovaleryl chloride [13] (0.2 g) in dry dichloromethane (5 ml) at 0 °C. The solution was then stirred for 20 h at room temperature, and then diluted with ethyl acetate. The solution was washed in turn with water, sodium hydrogen carbonate solution, water, and finally with saturated brine. The crude product was methylated with iodomethane and potassium carbonate in dry *NN*-dimethylformamide at room temperature. The crude product was purified by preparative t.l.c. (5% ethyl acetate–light petroleum) and crystallized from light petroleum as plates (74 mg) of 1-(1,3,7,9-*tetramethoxy*-2,6-*dimethyldibenzofuran*-4-*yl*)-3-*methylbutan*-1-*one* (29), m.p. 124—125 °C (Found: C, 69.0; H, 7.2. $C_{23}H_{28}O_6$ requires C, 69.0; H, 7.05%); δ ($CDCl_3$, 90 MHz) 1.03 (6 H, d, *J* 6.6 Hz, $CHMe_2$), 2.32 (6 H, s, 2 × ArMe), 2.32 (1 H, m, $CHMe_2$), 2.97 (2 H, d, *J* 7.0 Hz, $COCH_2$), 3.82, 3.86, 3.91, and 4.03 (each 3 H, s, OMe), and 6.44 (1 H, s, ArH); irradiation at δ 2.32 caused collapse of the $CHMe_2$ and the $COCH_2$ signals to singlets; *m/z* 401 (21.3%), 400 (84.1, M^+), 344 (21.3), 343 (100), 285 (10), 171.5 (23.8), 157 (14.3), 128 (15.6), 127 (11.7), and 115 (13.3).

(*b*) The substrate (9) (1.04 g) was allowed to react with tin(IV) chloride and isovaleryl chloride for 65 h. The crude product was chromatographed over silica gel with 5—10% ethyl acetate–light petroleum as eluant. 1-(3-*Hydroxy*-1,7,9-*trimethoxy*-2,6-*dimethyldibenzofuran*-4-*yl*)-3-*methylbutan*-1-*one* (30) (1.15 g) crystallized from light petroleum (charcoal) as laths, m.p. 121—123 °C (Found: C, 68.3; H, 6.85. $C_{22}H_{26}O_6$ requires C, 68.4; H, 6.8%); δ ($CDCl_3$, 90 MHz) 1.01 (6 H, d, *J* 6.5 Hz, Me_2CH), 2.25 and 2.29 (each 3 H, s, ArMe), 2.27 (1 H, m, $CHMe_2$), 2.97 (2 H, d, *J* 7.0 Hz, $COCH_2$), 3.82, 3.88, and 4.03 (each 3 H, s, OMe), 6.35 (1 H, s, ArH), and 8.87 (1 H, s, D_2O exchangeable OH); irradiation at δ 2.27 caused collapse of the $CHMe_2$ and the $COCH_2$ signals to singlets; *m/z* 386 (32.1%, M^+), 330 (18.1), 329 (100), 302 (10.5), 271 (10.5), 164.5 (15.8), and 157 (12.3).

1-(1,3,7,9-*Tetrahydroxy*-2,6-*dimethyldibenzofuran*-4-*yl*)-3-*methylbutan*-1-*one* (31).—Boron tribromide (1.2 g) in dry dichloromethane (15 ml) was added in drops to a stirred solution of the dibenzofuranol (30) (205 mg) in dry dichloromethane (15 ml) with cooling in ice and salt. The mixture was stirred for 4.5 h without further addition of ice to the bath when examination of a small portion of the mixture by t.l.c. (silica gel; benzene–dioxan–acetic acid, 36 : 9 : 1) revealed only one mobile spot. The mixture was cooled to 0 °C and water and ethyl acetate were added with stirring. Extraction with more ethyl acetate gave an orange solution which gradually faded to yellow on shaking with water and then with saturated brine. The *dibenzofuran* (31) (171 mg) formed yellow needles (from methanol), m.p. 250—260 °C decomp. with browning from 240 °C (Found: C, 60.05; H, 6.1. $C_{19}H_{20}O_6 \cdot 2H_2O$ requires C, 60.0; H, 6.35%); δ ($CDCl_3$ and 1 drop CD_3SOCD_3, 80 MHz) 1.06 (6 H, d, *J* 6.3 Hz, Me_2CH), 2.12 and 2.30 (each 3 H, s, ArMe), 2.21 (1 H, m, $CHMe_2$), 3.12 (2 H, d, *J* 7.4 Hz, $COCH_2$), 6.49 (1 H, s, ArH), and 13.85 (1 H, s, OH); *m/z* 345 (20.1%), 344 (85.7, M^+), 343 (11.6), 329 (45.4), 311 (18.4), 302 (16.4), 288 (17.6), 287 (100), 260 (14.6), 143 (22.9), 128 (10.5), and 115 (10.5). It was insoluble in aqueous sodium hydrogen carbonate but gave a yellow solution in aqueous sodium carbonate.

1,1′-(1,3,7,9-*Tetrahydroxy*-2,6-*dimethyldibenzofuran*-4,8-*diyl*)-3,3′-*dimethyldibutan*-1-*one* (17).—The dibenzofuran (31) (50 mg) was dissolved in isovaleric acid (1.5 ml) and boron trifluoride–diethyl ether (1.5 ml) and heated on a steam-bath for 3 h. The cooled solution was diluted with water and extracted with ethyl acetate and the extract was washed successively with saturated sodium hydrogen carbonate, water, and finally with saturated brine. The crude product was heated under reflux in ethanol (50 ml) for 0.5 h and then subjected to preparative t.l.c. (30% ethyl acetate–light petroleum). The *dibenzofuran* (17) (8.0 mg), homogeneous on t.l.c., formed yellow needles (from ethyl acetate–light petroleum), m.p. 209—211 °C (Found: M^+, 428.1823. $^{12}C_{24}{}^1H_{28}{}^{16}O_7$ requires *M*, 428.1835); δ ($CDCl_3$, 80 MHz) 1.02 and 1.06 (each 6 H, d, *J* 6.9 Hz, Me_2CH), 2.12 and 2.30 (each 3 H, s, ArMe), 2.21 (2 H, m, Me_2CH), 3.11 (4 H, d, *J* 6.9 Hz, $COCH_2$), 3.25 and 7.37 (each 1 H, b, OH), and 13.84 and 13.93 (each 1 H, s, OH); *m/z* 429 (18.5%), 428 (73.4, M^+), 395 (13.8), 372 (25.8), 371 (100), 353 (30), 169 (13.4), 157 (26.9), and 115 (11.1). The tetra-acetate (pyridine, acetic anhydride, 25 °C, 24 h) was purified by preparative t.l.c. (20% ethyl acetate–light petroleum) and was obtained as a thick oil, homogenous on t.l.c.; δ ($CDCl_3$, 60 MHz) 0.97 and 1.01 (each 6 H, d, *J* 7 Hz, $CHMe_2$), 2.04 and 2.39 (each 3 H, s, ArMe), 2.30 (12 H, s, 4 × MeCO), and 2.62 and 3.00 (each 2 H, d, *J* 8 Hz, $COCH_2$); the $CHMe_2$ resonance was obscured by the $COMe$ signal; *m/z* 596 (0.9%, M^+), 554 (4.2), 512 (11), 470 (10.9), 429 (12.0), 428 (41.9), 371 (17), and 43 (100).

1-(1,3,7,9-*Tetramethoxy*-4,6-*dimethyldibenzofuran*-2-*yl*)-3-*methylbutan*-1-*one* (32).—Isovalerylation and subsequent methylation of compound (15) in the same manner as described for compound (9) gave a crude product which after preparative t.l.c. (5% ethyl acetate–light petroleum) crystallized from light petroleum as clusters of needles (65%) of the *dibenzofuran* (32), m.p. 165—167 °C (Found: C, 69.05; H, 7.25. $C_{23}H_{28}O_6$ requires C, 69.0; H, 7.05%); δ ($CDCl_3$, 90 MHz) 1.01 (6 H, d, *J* 6.4 Hz, Me_2CH), 2.35 and 2.44 (each 3 H, s, ArMe), 2.39 (1 H, m, $CHMe_2$), 2.79 (2 H, d, *J* 6.7 Hz, $COCH_2$), 3.79, 3.87, 3.93, and 4.01 (each 3 H, s, OMe), and 6.43 (1 H, s, ArH); irradiation at δ 2.39 caused collapse of the Me_2CH and the $COCH_2$ signals to singlets; *m/z* 401 (11.7%), 400 (43.6, M^+), 344 (21.3), 343 (100), 313 (13.7), 171.5 (12.9), 164 (11.5), and 115 (11.9).

1-(1,3,7,9-*Tetrahydroxy*-4,6-*dimethyldibenzofuran*-2-*yl*)-3-*methylbutan*-1-*one* (33).—Compound (15) (100 mg) was isovalerylated as above and the crude product in dry dichloromethane (8 ml) was stirred and treated at −10 °C with boron tribromide (600 mg) in dichloromethane (7.5 ml). The

Table 1. Atom co-ordinates (15)

Atom	Part a			Part b		
	x	*y*	*z*	*x*	*y*	*z*
C(1)	0.874 2(2)	0.434 8(3)	1.130 8(3)	0.579 3(2)	0.244 1(2)	0.835 2(3)
O(1)	0.817 6(2)	0.534 2(2)	1.081 8(3)	0.582 0(2)	0.381 1(2)	0.842 7(3)
C(11)	0.883 4(4)	0.679 1(3)	1.157 2(5)	0.473 7(4)	0.413 8(4)	0.748 7(6)
H(11A)	0.895(3)	0.711(4)	1.286(5)	0.454(3)	0.364(4)	0.623(5)
H(11B)	0.978(3)	0.689(3)	1.138(4)	0.401(4)	0.398(4)	0.793(5)
H(11C)	0.818(3)	0.728(3)	1.103(5)	0.488(4)	0.510(5)	0.771(5)
C(2)	0.995 7(3)	0.465 8(3)	1.247 3(3)	0.475 0(3)	0.132 9(3)	0.729 2(3)
H(2)	1.052(3)	0.559(3)	1.299(4)	0.400(2)	0.147(2)	0.663(3)
C(3)	1.048 1(2)	0.358 5(3)	1.291 9(3)	0.479 0(2)	−0.005 9(3)	0.727 6(3)
O(3)	1.169 4(2)	0.386 3(2)	1.405 0(3)	0.377 5(2)	−0.117 9(2)	0.625 4(2)
C(31)	1.242 8(3)	0.528 3(4)	1.463 1(6)	0.267 0(3)	−0.086 8(4)	0.530 6(5)
H(31A)	1.258(3)	0.551(4)	1.359(5)	0.230(3)	−0.020(3)	0.614(4)
H(31B)	1.199(4)	0.602(4)	1.537(5)	0.291(3)	−0.055(4)	0.449(5)
H(31C)	1.326(3)	0.521(3)	1.531(4)	0.206(3)	−0.175(3)	0.471(4)
C(4)	0.984 6(2)	0.217 3(3)	1.228 4(3)	0.581 0(2)	−0.041 9(2)	0.823 7(3)
C(41)	1.040 8(4)	0.100 7(4)	1.276 9(5)	0.585 8(4)	−0.191 9(3)	0.818 5(5)
H(41A)	1.109(4)	0.080(4)	1.233(5)	0.647(4)	−0.202(4)	0.918(6)
H(41B)	1.000(4)	0.008(5)	1.198(6)	0.627(4)	−0.244(4)	0.736(6)
H(41C)	1.030(4)	0.099(4)	1.378(5)	0.526(5)	−0.226(5)	0.865(7)
C(5)	0.866 0(2)	0.193 4(2)	1.115 0(3)	0.677 9(2)	0.072 7(3)	0.926 4(3)
O(5)	0.788 2(2)	0.057 8(2)	1.034 8(2)			
C(6)	0.806 2(2)	0.292 1(2)	1.060 0(3)	0.683 5(2)	0.213 6(2)	0.937 9(3)

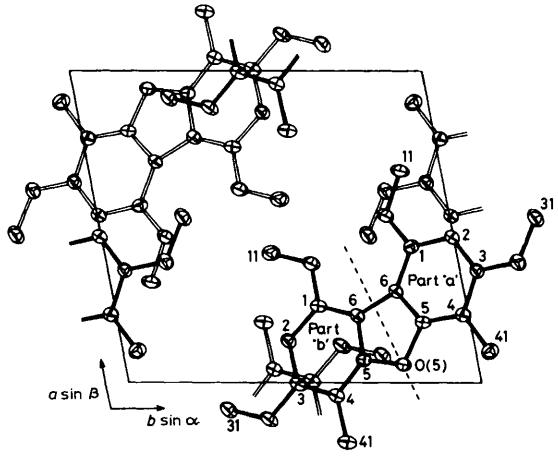


Figure 1. Unit cell contents of (15) projected down *c*. 20% Thermal ellipsoids are shown for the non-hydrogen atoms and crystallographic labelling for the carbon atom is given

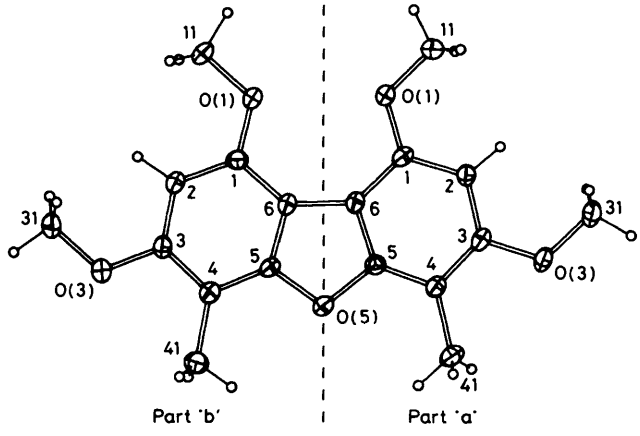


Figure 2. A molecule of (15) projected normal to the skeletal plane. Hydrogen atoms have an arbitrary radius of 0.1 Å

solution was stirred, without further addition of ice to the cooling bath, for 18 h. Work-up as described above for compound (31) gave a crude product which was subjected to preparative t.l.c. (50% ethyl acetate–light petroleum) and crystallization from ether–light petroleum then gave the *dibenzofuran* (33) (52 mg) as yellow needles, m.p. 224—226 °C (Found: C, 62.7; H, 5.95. $C_{19}H_{20}O_6 \cdot H_2O$ requires C, 62.95; H, 6.1%); δ ($CDCl_3$ and 1 drop CD_3SOCD_3, 80 MHz) 1.00 (6 H, d, *J* 6.3 Hz, CH*Me*$_2$), 2.30 and 2.31 (each 3 H, s, ArMe), 2.42 (1 H, m, C*H*Me$_2$), 3.10 (2 H, d, *J* 6.9 Hz, COC*H*$_2$), 6.47 (1 H, s, ArH), 8.28 (1 H, b, OH), 10.39 (2 H, b, 2 × OH), and 13.80 (1 H, s, OH); *m/z* 345 (11.6%), 344 (50.7, M^+), 311 (41.4), 288 (16.4), 287 (100), and 143.5 (12.5).

1,1′-(1,3,7,9-*Tetrahydroxy*-4,6-*dimethyldibenzofuran*-2,8-*diyl*)-2,3′-*dimethyldibutan*-1-*one* (2).—The dibenzofuran (33) was allowed to react with 2-methylbutyric acid and boron trifluoride–diethyl ether in the manner described for compound (31). Preparative t.l.c. (25% ethyl acetate–light petroleum) of the crude product gave the *dibenzofuran* (2) (75%) as yellow prisms (from chloroform–light petroleum), m.p. 199—201 °C homogeneous on t.l.c. (Found: M^+, 428.181 6. $^{12}C_{24}{}^{1}H_{28}{}^{16}O_7$ requires *M*, 428.1835); δ ($CDCl_3$, 80 MHz) 1.03 (3 H, t, *J* 7.1 Hz, CH_2Me), 1.08 (6 H, d, *J* 6.3 Hz, CH*Me*$_2$), 1.30 [3 H, d, *J* 6.9 Hz, CH(*Me*)Et], *ca.* 1.4—1.0 [3 H, m, $COCH_2 \cdot CHMe$ and $COCH(Me)CH_2Me$], 2.32 (6 H, s, 2 × ArMe), 3.16 (2 H, d, *J* 6.3 Hz, $COCH_2 \cdot CHMe_2$), 3.8—4.2 [1 H, m, COC*H*(Me)Et], 9.7—10.2 (2 H, b, 2 × OH), and 13.7—14.7 (2 H, b, 2 × OH); *m/z* 429 (13.9%), 428 (65.6, M^+), 395 (12.5), 372 (25.7), 371 (100), 353 (57.6), 169 (13.8), 157 (11.8), 128 (13.0), and 115 (13.9). The *tetra-acetate* formed needles (from ethyl acetate–light petroleum), m.p. 194—195 °C (Found: C, 64.3; H, 6.25. $C_{32}H_{36}O_{11}$ requires C, 64.4; H, 6.1%); δ ($CDCl_3$, 80 MHz) 0.94 (3 H, t, *J* 7.1 Hz, CH_2Me), 0.98 (6 H, d, *J* 6.3 Hz, CH*Me*$_2$), 1.15 [3 H, d, *J* 6.9 Hz, CH(*Me*)Et], *ca.* 1.3—1.0 [3 H, m, $COCH_2CHMe$ and $COCH(Me)CH_2Me$], 2.29 (6 H, s, 2 × ArMe), 2.31 and 2.38 (each 6 H, s, 2 × COMe), 2.66 (2 H, d, *J* 6.3 Hz, $COCH_2CHMe_2$), and 2.90

[1 H, m, COC*H*(Me)Et]; *m/z* (1%, M^+), 554 (2.3), 512 (4.9), 470 (16.6), 428 (32.9), 410 (17.2), 371 (12.0), 353 (11.7), and 43 (100%).

Attempted Degradation of 1-(1,3,7,9-*Tetrahydroxy*-2,6-*dimethyldibenzofuran*-4-*yl*)-3-*methylbutan*-1-*one* (31).—The dibenzofuran (31) (60 mg), and 10% aqueous sodium hydroxide (50 ml), which had been purged with nitrogen, were heated under reflux under dry nitrogen for 18 h. The cooled solution was diluted with water and acidified, and extracted exhaustively with ethyl acetate. The extract was washed in turn with sodium hydrogen carbonate solution, water, and saturated brine. The crude product was methylated with iodomethane and potassium carbonate in dry *NN*-dimethylformamide under dry nitrogen. The crude product was analysed using a Hewlett-Packard 5986 g.l.c.-mass spectrometer system with a 0.33 mm i.d. × 25 m OV-101 wall-coated open tubular capillary column at a helium flow rate of 7.5 ml min^{-1}, an injector temperature of 200 °C, and a column temperature of 160 °C rising at 20 °C min^{-1} to 240 °C after a delay of 1 min. Under these conditions compounds (32) and (29) had retention times of 12.1 and 13.8 min. The crude product contained only compound (29) and a contaminant with retention time 14.5 min and M^+ at *m/z* 384. Compounds (13) and (15) could not be detected in the crude product by t.l.c. or by ^1H n.m.r. spectroscopy.

Crystallography

Crystal Data.—$C_{18}H_{20}O_5$, *M* 316.4, Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), *a* 10.713(7), *b* 10.062(5), *c* 8.040(4) Å, α 109.36(4), β 100.15(5), γ 96.80(4)°, *U* 790.1(7) Å^3, D_m 1.35(1), D_c (*Z* = 2) 1.33 g cm^{-3}. *F*(000) 336. Monochromatic Mo-K_α radiation, λ 0.7106$_9$ Å, μ_{Mo} 1.0 cm^{-1}; *T* 295(1) K.

Structure Determination.—A unique data set was measured to the limit $2\theta_{max.} = 50°$, using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ/θ scan mode, yielding 2 627 independent reflections, 1 835 of which with $I > 3\sigma(I)$ were considered 'observed' and used in the full matrix least-squares refinement without absorption correction, after solution of the structure by direct methods. Hydrogen atoms (*x*,*y*,*z*, *U*) were refined; for the non-hydrogen atoms, anisotropic thermal parameters were refined. Residuals at convergence were (*R*,*R'*) 0.051, 0.064, reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral atom scattering factors were used, those for C,O being corrected for anomalous dispersion (*f'*,*f''*).[14] Computation used the X-RAY 76 program system implemented on a Perkin-Elmer 3240 computer by S. R. Hall.[15] Material deposited comprises structure factor amplitudes, thermal parameters, and hydrogen atom geometries.* Atom numbering employed is as follows; hydrogen atoms are numbered according to the parent carbon, suffixed A,B,C for distinguishing purposes in the case of the methyl hydrogens. (The molecule is divided into two sections a,b to facilitate tabulation and comparison of the geometry.)

Structural Commentary.—The structure determination of (15) establishes the stoicheiometry and stereochemistry as given above. One molecule comprises the asymmetric unit of the structure. The substituent disposition is such, however, that the overall molecular symmetry is a good approximation to *mm*, although the molecule contains no crystallographically imposed symmetry. The non-hydrogen skeleton of the molecule is closely planar; for a least-squares plane defined by the ring skeletons, σ is 0.01 Å, with none of the substituent atoms deviating by more than 0.20 Å [C(31A)].

The molecular geometry is compared with that of the parent dibenzofuran in Table 2. In most respects, it is closely similar, but non-trivial significant differences are found in respect of C(6)-C(6'), and a number of the aromatic ring angles; the differences in the latter may be reasonably attributed to substituent effects. In respect of the latter, the usual exocyclic angle distortions are observed.

Table 2. Molecular non-hydrogen geometry. The two values in each entry correspond to parts a, b. Values for the parent dibenzofuran are also given.

Atoms	Dibenzofuran *	Compound (15)
Distances/Å		
O(1) · · · O(1')		2.801(3)
C(1)–O(1)		1.358(4), 1.357(3)
C(1)–C(2)	1.38$_8$	1.396(4), 1.401(3)
C(1)–C(6)	1.38$_6$	1.407(3), 1.395(4)
O(1)–C(11)		1.418(3), 1.404(5)
C(2)–C(3)	1.38$_1$	1.393(4), 1.397(4)
C(3)–C(4)	1.38$_6$	1.382(3), 1.380(4)
C(3)–O(3)		1.386(3), 1.381(3)
O(3)–C(31)		1.429(4), 1.417(4)
C(4)–C(5)	1.39$_3$	1.371(4), 1.369(3)
C(4)–C(41)		1.509(5), 1.503(4)
C(5)–C(6)	1.38$_7$	1.390(4), 1.383(4)
C(5)–O(5)		1.389(3), 1.394(3)
C(6)–C(6')	1.48$_1$	1.450(3)
Angles/°		
C(2)–C(1)–O(1)		123.9(2), 122.2(2)
C(6)–C(1)–O(1)		118.0(2), 118.7(2)
C(2)–C(1)–C(6)	118.$_2$	118.1(3), 119.1(2)
C(1)–O(1)–C(11)		118.4(2), 118.8(2)
C(1)–C(2)–C(3)	121.$_7$	120.9(2), 119.1(2)
C(2)–C(3)–C(4)	121.$_2$	123.3(2), 124.0(2)
C(2)–C(3)–O(3)		122.0(2), 120.6(2)
C(4)–C(3)–O(3)		114.8(2), 115.4(2)
C(3)–O(3)–C(31)		116.8(3), 118.2(2)
C(3)–C(4)–C(5)	116.$_0$	113.2(2), 113.5(2)
C(3)–C(4)–C(41)		123.5(2), 123.7(2)
C(5)–C(4)–C(41)		123.4(2), 122.8(3)
C(4)–C(5)–C(6)	123.$_5$	128.0(2), 127.1(2)
C(4)–C(5)–O(5)	124.$_3$	121.8(2), 121.8(2)
C(6)–C(5)–O(5)	112.$_6$	110.2(2), 111.0(2)
C(5)–O(5)–C(5)	104.$_3$	106.2(2)
C(5)–C(6)–C(1)	119.$_3$	116.6(2), 117.2(2)
C(1)–C(6)–C(6)	135.$_1$	136.7(2), 137.0(2)
C(5)–C(6)–C(6)	105.$_5$	106.8(2), 105.8(2)

* Values are the mean of those given in O. Dideberg, L. Dupont, and J. M. André, *Acta Crystallogr., Sect. B*, 1972, **28**, 1002; and A. Banerjee, *Acta Crystallogr., Sect. B*, 1973, **29**, 2070.

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