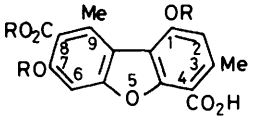
# Naturally Occurring Dibenzofurans. Part 2.[1] The Synthesis of Schizopeltic Acid

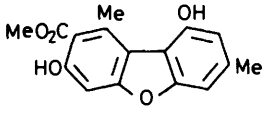
By **Melvyn V. Sargent** * and **Peter O. Stransky**, Department of Organic Chemistry, University of Western Australia, Nedlands, Western Australia, 6009, Australia

The structure of schizopeltic acid as 1,7-dimethoxy-8-methoxycarbonyl 3,9-dimethyldibenzofuran-4-carboxylic acid (1) has been confirmed by rational synthesis. 6-Methoxy-4-methylbenzofuran-2-carbaldehyde (10), available from 3,5-dimethoxytoluene (4) in six steps, was converted into methyl 1-acetoxy-7-methoxy-9-methyldibenzofuran-3-carboxylate (12) by Wittig reaction with 2-carboxy-1-methoxycarbonylethyltriphenylphosphorane and subsequent ring-closure of the resultant (*E*)-3-methoxycarbonyl-4-(6-methoxy-4-methylbenzofuran-2-yl)-but-3-enoic acid (11) with acetic anhydride. Reduction of compound (12) gave 7-methoxy-3,9-dimethyldibenzofuran-1-ol (14) which was converted into schizopeltic acid (1) by sequential formylations and oxidations.

THE dibenzofuran schizopeltic acid (1) was isolated from the lichens *Schizopelte californica* Th.Fr.,[2] *Reinkella parishii* Hasse,[2,3] and *Roccellina luteola* Follm.[4] A partial structural assignment followed from its conversion into derivatives of the known lichen dibenzofuran pannaric acid (2).[2,3] The location of the carboxy-group



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



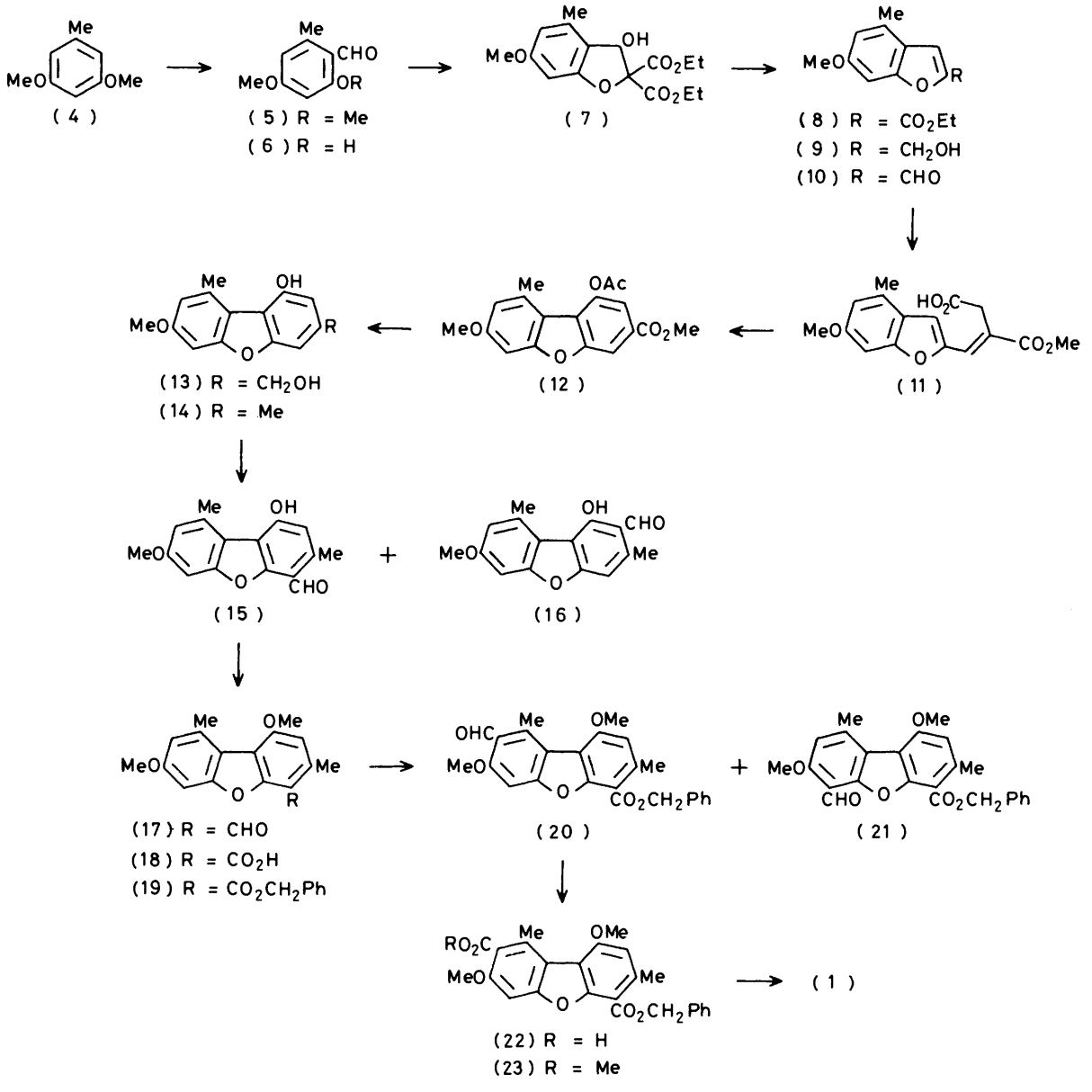
(3)

depended on application of the Gibbs test.[4] Thus, decarboxylation and subsequent boron tribromide-induced demethylation of schizopeltic acid gave a methyl dihydroxydibenzofurancarboxylate which gave a positive Gibbs test. Hence, one hydroxy-group in the latter compound must possess a free *para*-position and thus structure (3) is indicated, and structure (1) follows for schizopeltic acid. We have now confirmed this structural assignment by a rational synthesis of schizopeltic acid.

Any synthesis of schizopeltic acid must seek to differentiate the two carboxy-groups and we argued that the ring bearing the hydroxy-group in the *O*-methylpannarol (14) (see Scheme) would be more prone to undergo electrophilic substitution than the other benzenoid ring. Hence, the carboxy-groups could be introduced in turn and thereby differentiated. For the synthesis of the *O*-methylpannarol (14) we adopted a similar method to that used in our synthesis of cannabifuran.[1] The known benzofuran-2-carbaldehyde (10)[5] was thus required. This was readily obtained from everninaldehyde (6) which is most conveniently prepared by Vilsmeier–Haack formylation of 3,5-dimethoxytoluene (4) and subsequent boron trichloride-induced demethylation of the resultant di-*O*-methylorcylic aldehyde (5). Everninaldehyde (6) was allowed to react with diethyl bromomalonate and potassium carbonate in boiling acetone and the intermediate (7) was de-ethoxycarbonylated and dehydrated on being heated with lithium chloride in wet dimethyl sulphoxide to afford the ester (8). This was converted *via* the alcohol (9) into the aldehyde (10).

A Wittig reaction between the aldehyde (10) and 2-carboxy-1-methoxycarbonylethyltriphenylphosphorane[6] gave the itaconic half-ester (11) in high yield, and this cyclized to the dibenzofuran (12) on treatment with hot acetic anhydride. Reduction of this compound with lithium aluminium hydride gave the diol (13) which, on catalytic hydrogenation, afforded the *O*-methylpannarol (14). This compound failed to undergo Vilsmeier–Haack formylation with *NN*-dimethylformamide (DMF) and phosphoryl chloride ($POCl_3$) but it reacted smoothly with *N*-methylformanilide and phosphoryl chloride. This reaction gave a readily separable mixture of two aldehydes. The more soluble, minor isomer was assigned structure (16) since it exhibited a very-low-field deuterium oxide-exchangeable singlet, due to an intramolecularly hydrogen-bonded hydroxy-proton, in its $^1H$ n.m.r. spectrum. Further support for structure (16) came from the chemical shifts of the methyl protons. In the pannarol derivative (14) the methyl resonances occur at δ 2.39 and 2.87, that at lower field being assigned to the 9-methyl group because of the 1,9-steric interaction with the hydroxy-group. These assignments are compatible with the spectra of 1,7-dimethoxy-3,9-dimethyldibenzofuran, 1,9-dimethoxy-3,7-dimethyldibenzofuran, and 3,7-dimethoxy-1,9-dimethyldibenzofuran.[1] In compound (16) the 9-methyl group resonates at the same shift (δ 2.88) as in compound (14) but the resonance of the 3-methyl group is now deshielded by 0.25 p.p.m. due to the neighbouring carbonyl group. Similarly, the major aldehyde is assigned structure (15), formylation again having occurred on the more activated benzenoid ring. Thus, the chemical shifts of the 9-methyl groups are little altered on going from compound (14) to compound (15) or its methyl ether (17), but the 3-methyl group signals are deshielded by 0.22 and 0.37 p.p.m.

The methyl ether (17) of the major aldehyde was oxidized to the acid (18) with potassium permanganate in aqueous pyridine at 85 °C. The derived benzyl ester (19) was then subjected to formylation with dichloromethyl methyl ether and titanium tetrachloride at −10 °C. Some debenzylation occurred in this reaction and the crude product was rebenzylated. Again, two




SCHEME

easily separable aldehydes resulted. The major isomer was assigned structure (20). The $^1$H n.m.r. spectrum of the benzyl ester (19) exhibited methyl signals at δ 2.62 and 2.80; that at lower field again being assigned to the 9-methyl group. Irradiation of the 9-methyl group signal sharpened AB patterns at δ 6.72 (8-H) and 6.90 (6-H), and irradiation of the 3-methyl group signal sharpened a singlet at δ 6.58 (2-H). The $^1$H n.m.r. spectrum of the major aldehyde (20) exhibited signals due to aromatic protons at δ 6.63 and 6.95, and therefore assigned to the 2- and 6-protons. Irradiation of a methyl signal at δ 2.62 sharpened the 2-H resonance and irradiation of a methyl signal at δ 3.13 (deshielded by the *o*-formyl group) sharpened the 6-proton signal, thus supporting structure (20). In contrast, no additional deshielding of the 9-methyl-group signal (δ 2.85) in the $^1$H n.m.r. spectrum of the minor aldehyde occurred, hence the formyl group must be *para* to the 9-methyl group and this suggests structure (21) for the minor aldehyde. In keeping with this structure the dibenzofuran aromatic protons resonated at δ 6.59 (2-H) and 6.67 (8-H), the assignments being confirmed by double irradiation of the methyl group signals.

Oxidation of compound (20) with potassium permanganate in aqueous pyridine at 85 °C gave the crude acid (22) which was converted into its methyl ester (23). Hydrogenolytic debenzylation of this compound gave synthetic schizopeltic acid (1) which was identical with the natural product by the usual criteria, thus confirming the structural assignment of Huneck and his co-workers.[4]

## EXPERIMENTAL

General directions have been given before.[7] Light petroleum refers to that fraction boiling in the range 58—65 °C.

*2,4-Dimethoxy-6-methylbenzaldehyde* (5).—Phosphoryl chloride (17.5 ml) was added dropwise to a stirred solution of 3,5-dimethoxytoluene (4)[8] (25.0 g) in DMF (150 ml) at 0 °C. On completion of the addition the solution was stirred at room temperature for 15 h and then poured into water (750 ml). Next day the aldehyde (5) (26.5 g) was filtered off, washed with water, and dried *in vacuo*. A sample crystallised as felted needles (from light petroleum), m.p. 64—65 °C (lit.,[9] 64—65 °C); δ($CCl_4$, 60 MHz) 2.52 (3 H, s, Me), 3.81 and 3.87 (each 3 H, s, OMe), 6.13 (2 H, s, ArH), and 10.43 (1 H, s, CHO).

*2-Hydroxy-4-methoxy-6-methylbenzaldehyde* (6).—A solution of the crude aldehyde (5) (25.0 g) in anhydrous methylene dichloride (100 ml) was added over 2 h at −10 °C to a stirred solution of boron trichloride (55.0 g) in anhydrous dichloromethane (150 ml). After the addition the stirred solution was allowed to attain room temperature and was then poured cautiously into ice-cold water (600 ml). The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic extracts were filtered through Celite and then washed with brine. The crude product was filtered through a short plug of silica gel with 20% ethyl acetate–light petroleum as eluant to give, after work-up, everninaldehyde (6) (22.4 g). A sample crystallised as needles from methanol, m.p. 63—64 °C (lit.,[10] 63—64 °C).

*Diethyl 3-Hydroxy-6-methoxy-4-methyl-2,3-dihydrobenzofuran-2,2-dicarboxylate* (7).—Everninaldehyde (6) (22.25 g) and anhydrous potassium carbonate (42.5 g) were stirred in anhydrous acetone (300 ml) under dry nitrogen, and diethyl bromomalonate (37.0 g) was added dropwise. After the addition the mixture was stirred and heated under reflux for 12 h and the salts were then filtered off and washed with acetone. The combined washings and filtrate were evaporated under diminished pressure and the residue taken up in ethyl acetate and washed with water and then with saturated brine. The excess of the malonate was removed at 50 °C and 5 mmHg to give the *diester* (7) (43.5 g) as plates (from diethyl ether–light petroleum), m.p. 63—64 °C (Found: C, 59.2; H, 6.2%; $M^+$, 332. $C_{16}H_{20}O_7$ requires C, 59.2; H, 6.2%; *M*, 332); δ($CDCl_3$, 80 MHz) 1.27 and 1.35 (each 3 H, q, $CH_2Me$), 2.29 (1 H, d, *J* 8.9 Hz, $D_2O$-exchangeable OH), 2.35 (3 H, s, Me), 3.76 (3 H, s, OMe), 4.23 and 4.41 (each 2 H, t, $CH_2Me$), 5.85 (1 H, d, *J* 8.9 Hz, collapsing to a singlet on addition of $D_2O$, CHOH), and 6.38 (2 H, s, ArH).

*Ethyl 6-Methoxy-4-methylbenzofuran-2-carboxylate* (8).—The crude ester (7) (31.0 g) and lithium chloride (2.0 g) were heated at 165 °C (bath) in reagent-grade dimethyl sulphoxide (400 ml) for 2 h. The cooled mixture was poured into dilute hydrochloric acid and was extracted with ethyl acetate. The extract was washed with water and then with saturated brine. The crude product was filtered through a short plug of silica gel with 10% ethyl acetate–light petroleum as eluant to give, after work-up, the *ester* (8) (16.5 g) as needles (from light petroleum), m.p. 58—59 °C (Found: C, 66.5; H, 5.9%; $M^+$, 234. $C_{13}H_{14}O_4$ requires C, 66.65; H, 6.0%; *M*, 234); δ($CDCl_3$, 80 MHz) 1.41 (3 H, t, $CH_2Me$), 2.46 (3 H, s, Me), 3.82 (3 H, s, OMe), 4.41 (2 H, q, $CH_2Me$), 6.71 (1 H, narrow q, 5-H), 6.85br (1 H, m, 7-H), and 7.47 (1 H, d, $J_{3,7}$ 0.9 Hz, 3-H); on irradiation at δ 2.46 the 5-H signal appeared as a doublet, $J_{5,7}$ 2.0 Hz, and the 7-H signal appeared as a quartet, $J_{5,7}$ 2.0 and $J_{3,7}$ 0.9 Hz.

*6-Methoxy-4-methylbenzofuran-2-ylmethanol* (9).—A solution of the ester (8) (12.5 g) in anhydrous diethyl ether (150 ml) was added dropwise to a stirred mixture of lithium aluminium hydride (5.0 g) in anhydrous diethyl ether (200 ml). After the addition the mixture was stirred and heated under reflux for 0.5 h and then cooled to 0 °C and treated with an excess of saturated aqueous sodium sulphate. The usual work-up gave the *alcohol* (9) (10.0 g) as needles (from diethyl ether–light petroleum), m.p. 65 °C (Found: C, 68.55; H, 6.2%; $M^+$, 192. $C_{11}H_{12}O_3$ requires C, 68.75; H, 6.3%; *M*, 192); δ($CDCl_3$, 80 MHz) 2.13 (1 H, s, $D_2O$-exchangeable OH), 2.42 (3 H, s, Me), 3.80 (3 H, s, OMe), 4.69 (2 H, d, $J_{CH_2,3}$ 0.5 Hz, $CH_2OH$), 6.56br (1 H, s, 3-H), 6.66br (1 H, m, 5-H), and 6.80br (1 H, m, 7-H); on irradiation at δ 4.69 the 3-H signal appeared as a doublet, $J_{3,7}$ 1.0 Hz, and on irradiation at δ 2.43 the 5-H signal appeared as a doublet, $J_{5,7}$ 2.0 Hz, and the 7-H signal appeared as a quartet, $J_{5,7}$ 2.0 and $J_{3,7}$ 1.0 Hz.

*6-Methoxy-4-methylbenzofuran-2-carbaldehyde* (10).—The alcohol (9) (13.0 g) was stirred and heated under reflux in benzene (1.1 l) with activated manganese dioxide[11] (110 g) in a Dean–Stark apparatus for 2 h. The oxide was then filtered off and was washed with boiling ethyl acetate. Work-up of the filtrate and washings gave the aldehyde (10) (9.4 g) as needles (from methanol), m.p. 129—130 °C (lit.,[5] 129—130 °C).

*(E)-3-Methoxycarbonyl-4-(6-methoxy-4-methylbenzofuran-2-yl)but-3-enoic Acid* (11).—The aldehyde (10) (9.4 g) and 2-carboxy-1-methoxycarbonylethyltriphenylphosphorane[6] (21.0 g) were stirred together in anhydrous tetrahydrofuran (THF) (300 ml) for 5 d at room temperature. The solution was then poured into an excess of saturated aqueous sodium carbonate. The mixture was extracted with ethyl acetate and the extract was washed with saturated aqueous sodium carbonate. The combined carbonate solutions were acidified and the *acid* (11) (12.7 g) was extracted with ethyl acetate; it crystallised as prisms from diethyl ether, m.p. 145—146 °C (Found: C, 63.2; H, 5.4%; $M^+$, 304. $C_{16}H_{16}O_6$ requires C, 63.15; H, 5.3%; *M*, 304); δ($CDCl_3$, 80 MHz) 2.43 (3 H, s, Me), 3.80 and 3.82 (each 3 H, s, OMe), 4.01 (2 H, s, $CH_2$), 6.66br (1 H, s, 5′-H), 6.76br (1 H, s, 7′-H), 6.85 (1 H, s, 4-H), 7.60 (1 H, s, 3′-H) and 7.73br (1 H, $D_2O$-exchangeable OH).

*Methyl 1-Acetoxy-7-methoxy-9-methyldibenzofuran-3-carboxylate* (12).—A mixture of the acid (11) (12.0 g) and anhydrous sodium acetate (6.0 g) in acetic anhydride (300 ml) was heated on a steam-bath for 20 min. The solution was poured into water and when the acetic anhydride had hydrolysed a slight excess of sodium hydrogen carbonate was added. Extraction with ethyl acetate gave the *dibenzofuran* (12) (13.0 g) as needles (from diethyl ether–light petroleum), m.p. 166—167 °C (Found: C, 65.4; H, 4.85%; $M^+$, 328. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.9%; *M*, 328); δ($CDCl_3$, 80 MHz) 2.43 (3 H, s, COMe), 2.78 (3 H, s, 9-Me), 3.89 and 3.96 (each 3 H, s, OMe), 6.76br and 6.93br (total 2 H, AB, 8- and 6-H), and 7.73 and 8.07 (total 2 H, AB, $J_{2,4}$ 1.4 Hz, 2- and 4-H); irradiation at δ 2.78 sharpened the high-field AB pattern ($J_{6,8}$ 2.4 Hz).

*3-Hydroxymethyl-7-methoxy-9-methyldibenzofuran-1-ol* (13).—A solution of the ester (12) (12.4 g) in anhydrous THF (450 ml) was added dropwise to a stirred mixture of lithium aluminium hydride (5.0 g) in anhydrous THF (300

ml). The mixture was then stirred and heated under reflux for 0.5 h and then cooled to 0 °C and treated with an excess of saturated aqueous sodium sulphate. The usual work-up gave the *dibenzofuran*-1-*ol* (13) (8.5 g) as prisms (from ethyl acetate), m.p. 172—174 °C (Found: C, 69.35; H, 5.5%; $M^+$, 268. $C_{15}H_{14}O_9$ requires C, 69.75; H, 5.45%; *M*, 268).

7-*Methoxy*-3,9-*dimethyldibenzofuran*-1-*ol* (14).—A solution of the diol (13) (8.3 g) in deoxygenated methanol (400 ml) containing several drops of concentrated hydrochloric acid was stirred under hydrogen with 10% palladized charcoal (Engelhard, 1.0 g) until absorption ceased (2 d). The usual work-up gave the *dibenzofuran*-1-*ol* (14) (6.8 g) as prisms (from light petroleum), m.p. 134—135 °C (Found: C, 74.4; H, 5.9%; $M^+$, 242. $C_{15}H_{14}O_3$ requires C, 74.35; H, 5.8%; *M*, 242); δ($CDCl_3$, 80 MHz) 2.39 (3 H, s, 3-Me), 2.87 (3 H, s, 9-Me), 3.85 (3 H, s, OMe), 5.27 (1 H, s, $D_2O$-exchangeable OH), 6.43br and 6.90br (total 2 H, AB, 2- and 4-H), and 6.69br and 6.86br (total 2 H, AB, 8- and 6-H); irradiation at δ 2.39 sharpened the AB pattern due to 2- and 4-H ($J_{2,4}$ 1.4 Hz) and irradiation at δ 2.87 sharpened the AB pattern due to 6- and 8-H ($J_{6,8}$ 2.0 Hz).

*Formylation of Compound* (14).—Phosphoryl chloride (8.0 ml) was added to stirred *N*-methylformanilide (11.7 ml) at 0 °C. When the mixture had attained room temperature the dibenzofuranol (14) (7.0 g) was added in portions to the stirred mixture. The solution was stirred for 3 h at room temperature, and then cooled in ice and stirred with a mixture of water and ethyl acetate. Extraction with more ethyl acetate gave, after evaporation the crude product which was boiled with benzene. The benzene-insoluble material was filtered off and, on crystallisation from ethyl acetate, it afforded 1-*hydroxy*-7-*methoxy*-3,9-*dimethyldibenzofuran*-4-*carbaldehyde* (15) (3.2 g) as prisms, m.p. 250—260 °C (decomp.) (Found: C, 71.1; H, 5.25%); $M^+$, 270. $C_{16}H_{14}O_4$ requires C, 71.1; H, 5.2%; *M*, 270); δ[$(CD_3)_2SO$, 80 MHz] 2.61 and 2.83 (each 3 H, s, Me), 3.83 (3 H, s, OMe), 6.64 (1 H, s, 2-H), 6.76 and 7.10 (total 2 H, AB, *J* 2.0 Hz, 8- and 6-H), and 10.52 (1 H, s, CHO); irradiation at δ 2.61 sharpened the 2-H signal and irradiation at δ 2.83 sharpened the AB pattern.

The benzene–soluble material was chromatographed over silica gel with 2.5—15% ethyl acetate–light petroleum as eluant to afford, after work-up, 1-*hydroxy*-7-*methoxy*-3,9-*dimethyldibenzofuran*-2-*carbaldehyde* (16) (1.05 g) as yellow needles (from light petroleum), m.p. 137—138 °C (Found: C, 71.2; H, 5.25; $M^+$, 270. $C_{16}H_{14}O_4$ requires C, 71.1; H, 5.2%; *M*, 270); δ($CDCl_3$, 80 MHz) 2.64 and 2.88 (each 3 H, s, Me), 3.85 (3 H, s, OMe), 6.73 and 6.81 (total 2 H, AB, *J* 2.0 Hz, 8- and 6-H), 6.81 (1 H, s, 4-H), 10.23 (1 H, s, CHO), and 13.38 (1 H, s, $D_2O$-exchangeable OH).

1,7-*Dimethoxy*-3,9-*dimethyldibenzofuran*-4-*carbaldehyde* (17).—The aldehyde (15) (3.1 g) and potassium carbonate (3.3 g) were stirred with methyl iodide (1.0 ml) in DMF (100 ml) at room temperature for 3 h. The usual work-up gave the *aldehyde* (17) (3.0 g) as prisms (from light petroleum), m.p. 138—139 °C (Found: C, 71.95; H, 5.7%; $M^+$, 284. $C_{17}H_{16}O_4$ requires C, 71.8; H, 5.65%; *M*, 284); δ($CDCl_3$, 80 MHz) 2.76 and 2.80 (each 3 H, s, Me), 3.87 and 4.02 (each 3 H, s, OMe), 6.57 (1 H, s, 2-H), 6.73 and 6.95 (total 2 H, AB, *J* 2.0 Hz, 8- and 6-H), and 10.71 (1 H, s, CHO).

*Benzyl* 1,7-*Dimethoxy*-3,9-*dimethyldibenzofuran*-4-*carboxylate* (19).—A solution of the aldehyde (17) (3.7 g) in pyridine (25 ml) and water (20 ml) was stirred at 85 °C (bath) and powdered potassium permanganate (2.8 g) was added in portions over 20 min. The mixture was then poured into an excess of ice-cold dilute hydrochloric acid. The manganese dioxide which had formed was brought into solution by the addition of sodium disulphite ($Na_2S_2O_5$). Extraction with ethyl acetate, isolation with aqueous sodium carbonate, and precipitation with acid in the usual way gave the *carboxylic acid* (18) (3.0 g) as prisms (from diethyl ether), m.p. 218—221 °C (Found: C, 67.85; H, 5.2%; $M^+$, 300. $C_{17}H_{16}O_5$ requires C, 68.0; H, 5.35%; *M*, 300); δ[$(CD_3)_2$-SO, 80 MHz] 2.57 and 2.78 (each 3 H, s, Me), 3.83 and 3.94 (each 3 H, s, OMe), 6.76 and 7.10 (total 2 H, AB, *J* 2.0 Hz, 8- and 6-H), and 6.83 (1 H, s, 2-H). Benzylation of this compound with the calculated amount of benzyl bromide and an excess of potassium carbonate in DMF at room temperature gave the *benzyl ester* (19) as needles (from diethyl ether), m.p. 137—138 °C (Found: C, 73.9; H, 5.4%; $M^+$, 390. $C_{24}H_{22}O_5$ requires, C, 73.85; H, 5.7%; *M*, 390); δ($CDCl_3$, 80 MHz) 2.62 and 2.80 (each 3 H, s, Me), 3.86 and 3.98 (each 3 H, s, OMe), 5.48 (2 H, s, $CH_2$), 6.58 (1 H, s, 2-H), 6.72 and 6.90 (total 2 H, AB, *J* 2.0 Hz, 8- and 6-H), and 7.31—7.72 (5 H, m, Ph).

*Formylation of Compound* (19).—Titanium tetrachloride (0.15 ml) was added slowly at −10 °C to a stirred solution of the ester (19) (100 mg) and dichloromethyl methyl ether (0.2 ml) in dry methylene dichloride (4 ml). After 1 h at −10 °C the mixture was poured into water and extracted with ethyl acetate. The extract was washed with water and then with saturated brine. Evaporation of the extract gave a residue which was dissolved in anhydrous DMF (5 ml) and the solution was stirred at room temperature for 18 h with anhydrous potassium carbonate (150 mg) and benzyl bromide (60 μl). The crude product, obtained by the usual work-up, was boiled with diethyl ether (50 ml) and the insoluble material (24 mg) was filtered off. The material obtained by evaporation of the filtrate was subjected to preparative layer chromatography (p.l.c.) with chloroform–light petroleum (2 : 1 v/v) as developer. Two bands were obtained. The material from the faster band was combined with the aforementioned ether-insoluble material and the mixture was crystallised from ethyl acetate–light petroleum as needles (48 mg) of *benzyl* 8-*formyl*-1,7-*dimethoxy*-3,9-*dimethyldibenzofuran*-4-*carboxylate* (20), m.p. 165—167 °C (Found: C, 71.6; H, 5.2%; $M^+$, 418. $C_{25}H_{22}O_6$ requires C, 71.75; H, 5.3%; *M*, 418); δ($CDCl_3$, 80 MHz) 2.62 and 3.13 (each 3 H, s, Me), 3.95 and 3.99 (each 3 H, s, OMe), 5.49 (2 H, s, $CH_2$), 6.63 and 6.95 (total 2 H, 2 × s, 2- and 6-H), 7.36—7.70 (5 H, m, Ph), and 10.66 (1 H, s, CHO); irradiation at δ 2.62 sharpened the 2-H signal and irradiation at 3.13 sharpened the 6-H signal.

The slower band afforded needles (18 mg) of *benzyl* 6-*formyl*-1,7-*dimethoxy*-3,9-*dimethyldibenzofuran*-4-*carboxylate* (21) (from ethyl acetate–light petroleum), m.p. 177—178 °C (Found: C, 71.7; H, 5.4%; $M^+$, 418. $C_{25}H_{22}O_6$ requires C, 71.75; H, 5.3%; *M*, 418); δ($CDCl_3$, 80 MHz) 2.64 and 2.85 (each 3 H, s, Me), 3.96 (6 H, s, 2 × OMe), 5.50 (2 H, s, $CH_2$), 6.59 and 6.67 (total 2 H, 2 × s, 2- and 8-H), 7.36—7.76 (5 H, m, Ph), and 10.51 (1 H, s, CHO).

*Benzyl* 1,7-*Dimethoxy*-8-*methoxycarbonyl*-3,9-*dimethyldibenzofuran*-4-*carboxylate* (23).—A solution of the aldehyde (20) (160 mg) in pyridine (8 ml) and water (4 ml) was stirred at 85 °C (bath) and powdered potassium permanganate (140 mg) was added in portions over 20 min. Work-up as described above [for compound (18)] gave the crude acid (22) which was methylated with methyl iodide and potassium carbonate in DMF at room temperature. The

crude product was subjected to p.l.c. using 15% ethyl acetate–light petroleum as developer. The major band afforded *benzyl schizopeltate* (23) (105 mg) as needles (from ethyl acetate–light petroleum), m.p. 118—119 °C (Found: C, 69.5; H, 5.3%; $M^+$, 448. $C_{26}H_{24}O_7$ requires C, 69.65; H, 5.4%; *M*, 448); δ($CDCl_3$, 80 MHz) 2.62 and 2.78 (each 3 H, s, Me), 3.88, 3.95, and 3.98 (each 3 H, s, OMe), 5.48 (2 H, s, $CH_2$), 6.61 and 6.96 (total 2 H, 2 × s, 2- and 6-H), and 7.37—7.75 (5 H, m, Ph); irradiation at δ 2.62 sharpened the 2-H signal and irradiation at 2.78 sharpened the 6-H signal.

1,7-*Dimethoxy*-8-*methoxycarbonyl*-3,9-*dimethyldibenzofuran*-4-*carboxylic Acid* (*Schizopeltic Acid*) (1).—Benzyl schizopeltate (23) (20 mg) and 10% palladized charcoal (8 mg) were stirred in ethyl acetate (5 ml) containing concentrated hydrochloric acid (1 drop) under hydrogen until absorption ceased (15 min). The usual work-up gave *schizopeltic acid* (1) (15 mg) as needles (from methanol), m.p. 229—231 °C (lit.,[4] 229—231 °C) (Found: C, 63.6; H, 5.1. $C_{19}H_{18}O_7$ requires C, 63.7; H, 5.05%); δ($CDCl_3$, 80 MHz) 2.76 and 2.80 (each 3 H, s, Me), 3.90, 3.96, and 4.02 (each 3 H, s, OMe), and 6.68 and 7.05 (total 2 H, 2 × s, 2- and 6-H); irradiation at δ 6.68 sharpened the 3-Me signal and irradiation at 7.05 sharpened the 9-Me signal; mass spectrum (Hewlett-Packard 5986 instrument) *m/z* 359 (17.6%), 358 ($M^+$, 100), 328 (8.2), 327 (37.5), 312 (9.8), 311 (31.1), 155 (16.8), 141 (12.8), 139 (17.0), 133 (11.2), and 126 (17.6). Compound (1) was identical (mixed m.p., $R_F$ values in three different solvent systems, mass- and n.m.r.-spectra) with an authentic sample.

We thank Dr. J. A. Elix for the authentic sample of schizopeltic acid, and the Australian Research Grants Committee for financial support.

[2/190 *Received*, 1*st February*, 1982]

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