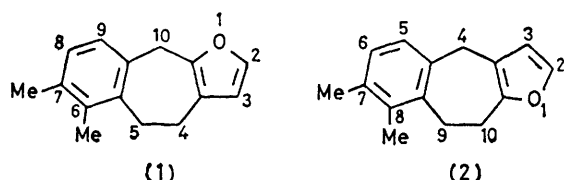


Structure and Synthesis of Pallescensin E Utilising a Modified Wadsworth–Emmons Reaction

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A modified Wadsworth–Emmons reaction using a catalytic amount of 15-crown-5 has been employed in the synthesis of the naturally occurring furosesquiterpene pallescensin E. The structure of this compound has been confirmed by comparison of its spectral data with those of the synthesised isomer, 9,10-dihydro-7,8-dimethyl-4*H*-benzo[4,5]cyclohepta[1,2-*b*]furan.

PALLESCENSIN E (1), a furosesquiterpene containing the monocyclofarnesyl skeleton, has been isolated from the marine sponge *Disidea pallescens*.¹ The structure (1) was proposed on the basis of spectral and chemical data¹ which failed, however, to distinguish structure (1) from its isomer (2),² and the decision in favour of the former was made on biogenetic grounds.¹ We report the total synthesis of compounds (1) and (2), and demonstrate that (1) is identical with naturally occurring pallescensin E. Furthermore, in this synthesis we have utilised a modification of the Wadsworth–Emmons procedure for olefin formation involving the addition of a catalytic quantity of crown ether to the reaction mixture.

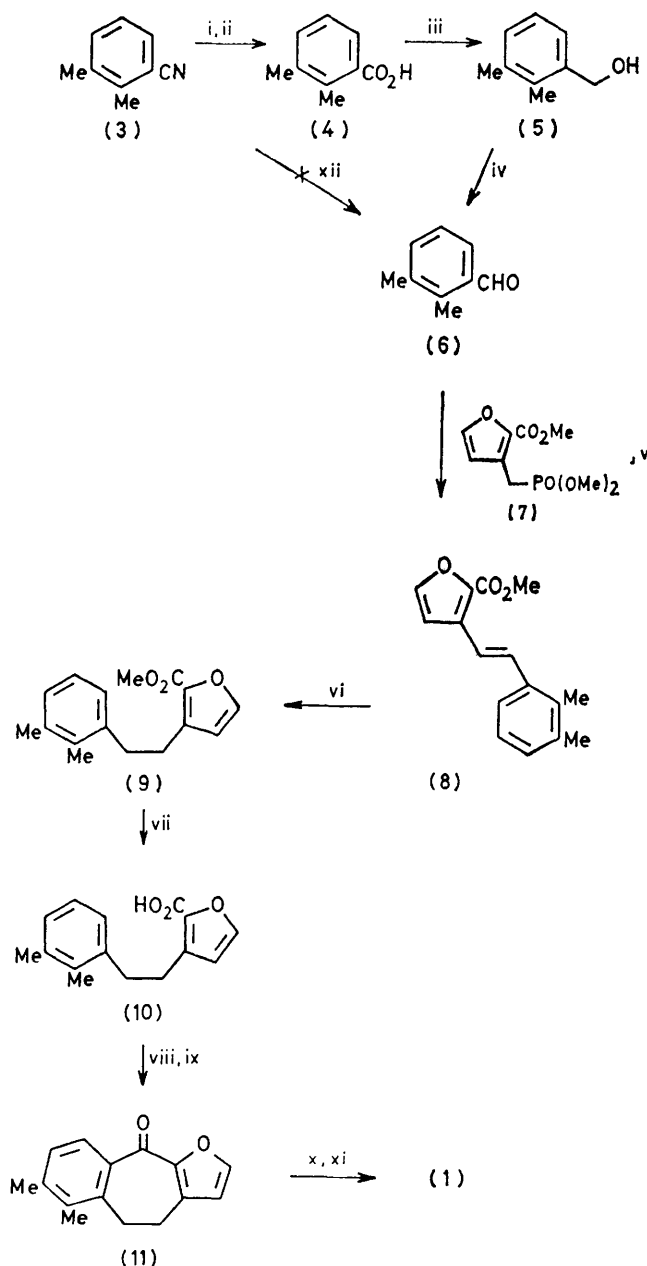


RESULTS AND DISCUSSION


The target compound (1) was synthesised as outlined in Scheme 1. Hydrolysis in basic media of the commercially available nitrile (3)² gave 2,3-dimethylbenzoic acid (4), which on reduction with lithium aluminium hydride gave the alcohol (5). Oxidation of the alcohol (5) with pyridinium chlorochromate gave 2,3-dimethylbenzaldehyde (6). This three-step route to (6) was used because direct Stephens reduction⁴ of the nitrile (3) did not yield the desired aldehyde (6).


No reaction could be achieved between the phosphonate (7) and the aldehyde (6), either under the conditions of Seus and Wilson⁵ or under a number of other literature conditions (*e.g.* NaOMe, 20–110 °C, Me₂NCHO).⁶ A study of the reaction of diethyl benzylphosphonate (12) with a number of aryl and furyl aldehydes and ketones showed that the addition of a catalytic quantity of crown ether greatly facilitated this reaction. Near quantitative yields of olefin products were obtained in short reaction times and at lower temperatures than those conventionally used (0–25 °C instead of 80 °C).^{6,7}


In the present study *trans*-stilbene (8) was obtained in 45% yield when a catalytic amount of 15-crown-5 was added to the reaction mixture containing the phos-



SCHEME 1 Reagents: i, KOH–H₂O; ii, HCl; iii, LiAlH₄–tetrahydrofuran; iv, pyridinium chlorochromate–CH₂Cl₂; v, NaH–(MeO[CH₂]₂)₂O–15-crown-5; vi, H₂–Rh(Ph₃P)₃Cl; vii, NaOH–H₂O; viii, SOCl₂–benzene; ix, AlCl₃–PhNO₂; x, TsNHNH₂–EtOH–TsOH; xi, NaCNBH₃–Me₂NCHO; xii, SnCl₄–EtOH

(12) 

(13) 

(14) 

The ^1H n.m.r. spectra of compounds (1) and (2) exhibited many similarities but were markedly different in two regions. The spectrum of (2) showed a broad singlet for the two 'dibenzyl' protons (C-4) at δ 3.57, whereas that of (1) showed a broad singlet for the 'dibenzyl' protons (C-10) at δ 3.91, in good agreement with the published value of 3.90 for pallascensin E.¹ The spectrum of (2) also showed a single, four-proton multiplet for the 'monobenzyl' protons (C-9 and C-10) at δ 2.72, whereas the spectrum of (1) showed a pair of two-proton multiplets, at δ 2.82 and 2.42, again in good agreement with the published values of 2.80 and 2.44 for pallescensin E.¹ The remaining spectral data for (1) were in good agreement with the published data.¹

(15) $\xrightarrow{\text{i, ii, (14)}}$ (16)

(16) $\xrightarrow{\text{iii}}$ (17)

(17) $\xrightarrow{\text{iv}}$ (18)

(18) $\xrightarrow{\text{v, vi}}$ (19)

(19) $\xrightarrow{\text{vii, viii}}$ (2)

(E)-Methyl 3-(2,3-Dimethylstyryl)furan-2-carboxylate (8).—A solution of dimethyl 2-methoxycarbonyl-3-furylmethylphosphonate (7) ¹⁵ (23.1 g, 0.093 mol), 2,3-dimethylbenz-

aldehyde (6) (13.5 g, 0.1 mol), and 15-crown-5 (50 mg, 0.2 mmol) in dry bis-(2-methoxyethyl) ether (50 ml) was added dropwise to a suspension of sodium hydride (50% dispersion in oil; 4.8 g, 0.1 mol) in the same solvent (150 ml) at 80 °C over 0.5 h. After stirring at 80 °C for 1 h, and at room temperature for 1 h, the orange suspension which resulted was poured into saturated aqueous sodium chloride (500 ml) and the mixture extracted with ether (3 × 200 ml). The combined extracts were washed with aqueous sodium hydrogen sulphite (10%; 2 × 50 ml) and saturated aqueous sodium chloride (2 × 100 ml), dried (MgSO₄), and evaporated *in vacuo* to give a brown oil which was distilled *in vacuo* to give the styrylfuran (8) as a pale yellow oil (11.5 g, 45%), b.p. 158–164° at 0.1 mmHg, which crystallised; m.p. 64–65° (Found: C, 74.9; H, 6.4. C₁₆H₁₆O₃ requires C, 75.0; H, 6.3%); λ_{max.} (EtOH) 302 (ε 11 900), 246 (10 700), and 213 nm (13 200); ν_{max.} (CCl₄ soln.) 1 710 cm⁻¹; δ_H(CCl₄) 2.27 (6 H, s, 2 ArCH₃), 3.86 (3 H, s, CO₂CH₃), 6.84 (1 H, d, *J* 2 Hz, furan β-H), 6.98–8.62 (6 H, m, furan α-H, CH=CH, 3 ArH); δ_C(C²HCl₃) 15.4, 20.6, 51.7, 109.5, 120.1, 124.3, 126.9, 129.9, 132.2, 132.6, 134.5, 136.1, 136.9, 139.7, 145.5, and 159.8; *m/z* 256 (*M*⁺, 82%), 197 (100), 182 (54), 169 (60), 153 (36), and 105 (36).

Methyl 3-(2,3-Dimethylphenethyl)furan-2-carboxylate (9).—A solution of the styrylfuran (8) (30.5 g, 0.12 mol) and chlorotris(triphenylphosphine)rhodium⁸ (1 g) in ethanol–benzene (1 : 1, 800 ml) was degassed with argon and then hydrogenated at 70 °C under 160 atm for 14 days. The solution was evaporated *in vacuo* to give a black oil, which was dissolved in ethanol (200 ml) and filtered through silica gel (Kieselgel GF 254, Type 60). The filtrate was evaporated *in vacuo* to give a mixture as a light brown oil, which was separated by flash column chromatography. Elution with ether–light petroleum (b.p. 40–60 °C) (1 : 4) gave the phenethylfuran (9) as colourless microcrystals (16.6 g, 54%), m.p. 34–36° (Found: C, 74.1; H, 7.1. C₁₆H₁₈O₃ requires C, 74.4; H, 7.0%), λ_{max.} (EtOH) 216 (ε 12 900) and 253 nm (12 600); ν_{max.} (film) 1 715 cm⁻¹; δ_H(C²HCl₃) 2.27 and 2.31 (6 H, 2 s, 2 ArCH₃), 2.74–3.17 (4 H, m, 2 CH₂), 3.89 (3 H, s, CO₂CH₃), 6.33 (1 H, d, *J* 2 Hz, furan β-H), 7.10 (3 H, br, s, 3 ArH), and 7.41 (1 H, d, *J* 2 Hz, furan α-H); δ_C(C²HCl₃) 14.9, 20.7, 26.8, 34.3, 51.6, 114.0, 125.5, 127.1, 128.0, 134.6, 135.3, 136.9, 139.3, 139.9, 145.0, and 159.8; *m/z* 258 (*M*⁺, 9%), 226 (5), 120 (10), 119 (100), 91 (6), and 77 (4).

3-(2,3-Dimethylphenethyl)furan-2-carboxylic Acid (10).—A solution of the ester (9) (0.80 g, 0.31 mol) in ethanol (10 ml) was treated with aqueous sodium hydroxide solution (10%; 50 ml) and boiled under reflux for 1 h. The mixture was cooled to room temperature, acidified with m-hydrochloric acid, cooled on ice, and filtered to give a white solid, which was crystallised from ethanol–water to yield the acid (10) as white microcrystals (0.53 g, 69%), m.p. 174–176° (Found: C, 73.5; H, 6.7. C₁₅H₁₆O₃ requires C, 73.8; H, 6.6%); λ_{max.} (EtOH) 245 (ε 11 800) and 215 nm (12 800); ν_{max.} (Nujol) 1 680 cm⁻¹; δ_H[(C²H₅)₂SO] 2.23 and 2.26 (6 H, 2 s, ArCH₃), 2.64–3.15 (4 H, m, 2 CH₂), 6.56 (1 H, d, *J* 2 Hz, furan β-H), 6.99 (3 H, br, s, 3 ArH), and 7.77 (1 H, d, *J* 2 Hz, furan α-H); δ_C[(C²H₅)₂SO] 14.5, 20.4, 26.5, 33.8, 114.0, 125.2, 126.8, 127.7, 134.2, 136.2, 139.3, 140.1, 145.3, and 160.3; *m/z* 244 (*M*⁺, 7%), 120 (8), 119 (100), 91 (6), 77 (3), and 41 (3).

5,10-Dihydro-6,7-dimethyl-4H-benzo[5,6]cyclohepta[1,2-b]-furan-10-one (11).—A suspension of the acid (10) (10.36 g, 0.042 mol) in benzene (300 ml) was treated with thionyl

chloride (6.3 ml, 10.3 g, 0.086 mol) and boiled under reflux for 2 h. The solvent was removed *in vacuo* to give an orange solid which was dissolved in nitrobenzene (300 ml). The resulting solution was cooled to 0 °C and aluminium chloride (15 g, 0.11 mol) added. The mixture was stirred at room temperature for 16 h, then at 80 °C for 4 h, poured into water, and extracted with ether (3 × 100 ml). The extracts were washed with aqueous sodium hydroxide (10%; 1 × 50 ml), saturated aqueous sodium hydrogen carbonate (1 × 50 ml), saturated aqueous sodium chloride (2 × 100 ml), and dried (MgSO₄). The extracts were evaporated *in vacuo* to leave a black oil which was concentrated to ca. 20 ml by distillation at reduced pressure. The residue was dissolved in ether–light petroleum (b.p. 40–60 °C) (1 : 4) and passed down a short silica column (2 in), and the solution was evaporated to give a brown oil (9 g) which crystallized. The solid mixture (3 × 3 g) was separated by flash column chromatography. Elution with ether–light petroleum (b.p. 40–60 °C) (1 : 4) gave the benzocycloheptafuranone (11) as colourless microcrystals (7.52 g, 78%), m.p. 143–145° (Found: C, 79.2; H, 6.1. C₁₅H₁₆O₃ requires C, 79.6; H, 6.2%); λ_{max.} (EtOH) 212 (ε 7 600), 279sh (7 200), 236 (3 600), and 306 nm (10 200); ν_{max.} (CHCl₃ soln.) 1 630 cm⁻¹; δ_H(C²HCl₃) 2.33 and 2.36 (6 H, 2 s, 2 ArCH₃), 2.70–2.96 (2 H, m, CH₂), 3.04–3.26 (2 H, m, CH₂), 6.46 (1 H, d, *J* 2 Hz, furan β-H), 7.08 (1 H, d, *J* 8 Hz, H-8), 7.50 (1 H, d, *J* 2 Hz, furan α-H), and 7.67 (1 H, d, *J* 8 Hz, H-9); δ_C(C²HCl₃) 15.9, 21.7, 25.2, 29.5, 113.4, 127.3, 128.5, 134.0, 136.9, 137.7, 141.8, 146.5, 149.3, and 181.9; *m/z* 226 (*M*⁺, 100%), 225 (31), 211 (25), 197 (21), 183 (21), and 155 (21).

5,10-Dihydro-6,7-dimethyl-4H-benzo[5,6]cyclohepta[1,2-b]-furan (1).—A mixture of the benzocycloheptafuranone (11) (1.0 g, 4.4 mmol), 4-tolylsulphonylhydrazine (0.82 g, 4.4 mmol) and toluene-4-sulphonic acid (50 mg) in ethanol (2 ml) was heated at 80 °C for 16 h. The solvent was removed from the resulting suspension *in vacuo* to yield a paste, which was dissolved in dimethylformamide (5 ml). To the resulting solution sodium cyanotrihydridoborate (1.0 g, 14.7 mmol) was added, and the mixture heated at 120 °C for 12 h, poured into water (100 ml) and extracted with ether–light petroleum (b.p. 40–60 °C) (1 : 4) (3 × 25 ml). The extracts were dried (K₂CO₃) and evaporated to give a mixture as a red oil (1.1 g) which was separated by flash column chromatography. Elution with light petroleum (b.p. 40–60 °C) gave a two-component mixture as an oil (920 mg) which was separated by flash column chromatography. Elution with light petroleum (b.p. 60–80 °C) gave the benzocycloheptafuran¹ (1) as a colourless oil (290 mg, 31%) (Found: *M*⁺, 212.1188. C₁₅H₁₆O requires *M*, 212.1201); λ_{max.} (EtOH) 217 nm (ε 12 600); δ_H(C₆H₆) 2.01 (3 H, s, ArCH₃), 2.10 (3 H, s, ArCH₃), 2.42 (2 H, m, CH₂), 2.82 (2 H, m, CH₂), 3.91 (2 H, br, s, furan CH₂Ar), 5.94 (1 H, d, *J* 2 Hz, furan β-H), 6.77 (2 H, s, 2 ArH), and 7.01 (1 H, d, *J* 2 Hz, furan α-H); *m/z* 213 (*M*⁺ + 1, 15%), 212 (*M*⁺, 95), 198 (15), 197 (100), 183 (14), and 167 (27).

Methyl 5-(2,3-Dimethylphenyl)-3-oxopentanoate (16).—A solution of dry methyl 3-oxobutanoate (15) (8.3 g, 0.07 mol) in anhydrous tetrahydrofuran (20 ml) was added dropwise to a suspension of sodium hydride (50% dispersion in oil; 3.36 g, 0.07 mol) in dry tetrahydrofuran (200 ml) at –5 °C.¹⁶ The mixture was stirred for 15 min at 0 °C and n-butyl-lithium (1.6M-solution in hexane; 43 ml, 0.069 mol) added dropwise; the yellow-orange solution was stirred for 15 min at 0 °C. A solution of 2,3-dimethyl-

benzyl bromide (14) ¹⁷ (14.3 g, 0.07 mol) in tetrahydrofuran (30 ml) was added over 5 min. The resulting pale yellow suspension was stirred at 0 °C for 15 min and at room temperature for 5 min. A solution of concentrated hydrochloric acid (14 ml) in water (35 ml) was added, and the suspension stirred for 2 min. The aqueous phase was separated and extracted with ether (2 × 25 ml). The combined extracts were washed with saturated aqueous sodium chloride (2 × 250 ml), dried (MgSO₄), and evaporated to give the *oxo-ester* (16) as a pale yellow oil (15.1 g, 92%). Distillation of 1.0 g *in vacuo* gave a colourless oil (0.75 g), b.p. 152° at 0.1 mmHg, which was subjected to flash column chromatography. Eluting with ether–light petroleum (b.p. 40–60 °C) (1 : 4) gave a colourless oil (0.52 g) (Found: C, 72.1; H, 7.6. C₁₄H₁₈O₃ requires C, 71.8; H, 7.7%; λ_{max} (EtOH) 214 (ϵ 10 600) and 248 nm (1 550); ν_{max} (film) 1 722 and 1 752 cm⁻¹; δ_{H} (C²HCl₃) 2.20 and 2.28 (6 H, 2 s, 2 ArCH₃), 2.26–3.10 (4 H, m, 2 CH₂), 2.44 (2 H, s, CCH₂CO₂CH₃), 3.72 (3 H, s, CO₂CH₃), and 7.05 (3 H, br, s, 3 ArH); m/z 234 (M^+ , 0.3%), 216 (29), 142 (47), 133 (32), 119 (100), 118 (48), 117 (23), and 91 (24).

Methyl 2-(2,3-Dimethylphenethyl)furan-3-carboxylate (17).—A mixture of the *oxo-ester* (16) (14.1 g, 0.06 mol), pyridine (4.8 ml, 4.7 g, 0.06 mol) and chloroacetaldehyde (50–55% solution in water; 9.5 ml) was stirred at room temperature for 16 h. The mixture was poured into saturated aqueous sodium chloride (200 ml) and extracted with ether (3 × 100 ml). The extracts were washed with saturated aqueous sodium chloride (2 × 50 ml), dried (MgSO₄), and evaporated to give a pale yellow oil (18.1 g), which was distilled *in vacuo* to yield the furan (17) as a colourless oil (11.5 g, 74%), b.p. 195° at 0.1 mmHg. Crystallisation from di-isopropyl ether gave colourless *microcrystals* m.p. 81–83° (Found: C, 74.1; H, 7.0. C₁₆H₁₈O₃ requires C, 74.4; H, 7.0%; λ_{max} (EtOH) 214 (ϵ 9 700) and 247 nm (6 200); ν_{max} (film) 1 712 cm⁻¹; δ_{H} (C²HCl₃) 2.26 and 2.29 (6 H, 2 s, 2 ArCH₃), 2.84–3.38 (4 H, m, 2 CH₂), 3.80 (3 H, s, CO₂CH₃), 6.64 (1 H, d, J 2 Hz, furan β -H), 7.01 (3 H, s, 3 ArH), and 7.26 (1 H, d, J 2 Hz, furan α -H); δ_{C} (C²HCl₃) 164.3, 162.2, 140.7, 138.9, 136.9, 128.2, 127.1, 125.5, 113.3, 110.8, 51.2, 32.6, 28.9, 20.7, and 14.8; m/z 259 (M^+ + 1, 2%), 258 (M^+ , 11%), 226 (10), 139 (5), 120 (10), and 119 (100).

2-(2,3-Dimethylphenethyl)furan-3-carboxylic Acid (19).—Aqueous potassium hydroxide (10%; 50 ml) and ethanol (5 ml) were added to a suspension of the ester (17) (10.5 g, 0.041 mol) in water (20 ml). The mixture was boiled under reflux for 1 h, cooled to room temperature, and set aside for 16 h. The solution was acidified with 2M-hydrochloric acid and filtered to give a yellow powder (8.1 g). The powder was crystallised from ethanol–water to yield the acid (19) as a light tan powder (5.5 g, 55%), m.p. 152–154° (decomp.) (Found: C, 73.5; H, 6.8. C₁₅H₁₆O₃ requires C, 73.8; H, 6.6%; λ_{max} (EtOH) 215 (ϵ 14 900), and 202 nm (6 800); ν_{max} (Nujol) 1 684 cm⁻¹; δ_{H} (C²HCl₃) 2.27 and 2.29 (6 H, 2 s, 2 ArCH₃), 3.00 (2 H, m, CH₂), 3.25 (2 H, m, CH₂), 6.70 (1 H, d, J 2 Hz, furan β -H), 7.01 (3 H, s, 3 ArH), and 7.30 (1 H, d, J 2 Hz, furan α -H); m/z 244 (M^+ , 7%), 226 (3), 120 (8), 119 (100), and 91 (8).

9,10-Dihydro-7,8-dimethyl-4H-benzo[4,5]cyclohepta[1,2-b]-furan-4-one (20).—A suspension of the acid (19) (4.21 g, 0.017 mol) in benzene (50 ml) was treated with thionyl chloride (1.4 ml, 1.63 g, 0.019 mol) and the mixture boiled under reflux for 1.5 h. The solvent was removed *in vacuo* to give an orange-brown paste, which was taken up in

nitrobenzene (200 ml); aluminium chloride (4.6 g, 0.034 mol) was added. The resulting mixture was stirred at 95–90 °C for 16 h, poured into water (300 ml), and extracted with ether (3 × 100 ml). The extracts were washed with saturated aqueous sodium hydrogen carbonate (2 × 50 ml) and saturated aqueous sodium chloride (1 × 100 ml). The extracts were dried (K₂CO₃) and evaporated to give a black oil. The oil was dissolved in ether (200 ml) and passed through a silica gel (Kieselgel GF254 Type 60) column (1 in × 4 in diam.); the solution was evaporated to give a brown oil. This oil was concentrated at 0.1 mmHg to ca. 5 ml and separated by flash column chromatography. Elution with ether–light petroleum (b.p. 40–60 °C) (1 : 4) gave the *benzocycloheptafulranone* (20) as colourless *microcrystals* (1.00 g, 26%), m.p. 79–81° (Found: C, 79.6; H, 6.3. C₁₅H₁₄O₂ requires C, 79.7; H, 6.2%; λ_{max} (EtOH) 215 (ϵ 19 400), 226sh (14 500, sh), 267 (9 900), and 395m (7 800); ν_{max} (Nujol) 1 638 cm⁻¹; δ_{H} (C²HCl₃) 2.31 and 2.34 (6 H, 2 s, ArCH₃), 2.92–3.30 (4 H, m, 2 CH₂), 6.83 (1 H, d, J 2 Hz, furan β -H), 7.10 (1 H, d, J 8 Hz, H-6), 7.26 (1 H, d, J 2 Hz, furan α -H), and 7.54 (1 H, d, J 8 Hz, H-5); δ_{C} (C²HCl₃) 15.8, 21.6, 27.2, 110.5, 123.8, 126.8, 128.6, 133.9, 136.4, 138.8, 141.2, 163.4, and 188.7; m/z 226 (M^+ , 100%), 225 (45), 211 (57), 183 (47), 169 (59), 155 (47), 115 (51), and 91 (41).

9,10-Dihydro-7,8-dimethyl-4H-benzo[4,5]cyclohepta[1,2-b]-furan (2).—A mixture of the *benzocycloheptafulranone* (20) (0.50 g, 2.21 mmol), 4-tolylsulphonylhydrazine (0.41 g, 2.21 mmol), and toluene-4-sulphonic acid (50 mg) was heated at 80 °C for 2.5 h. The solvent was removed from the resulting suspension *in vacuo* to give an orange paste, which was dissolved in dry dimethylformamide (3 ml). Sodium cyanotrihydroborate (0.48 g, 7.6 mmol) and toluene-4-sulphonic acid (20 mg) were added to the solution, and the mixture was heated at 120 °C for 8 h. The solution was left at room temperature for 16 h, poured into water (20 ml) and extracted with ether–light petroleum (b.p. 40–60 °C) (1 : 9) (3 × 10 ml). The extracts were washed with saturated aqueous sodium chloride (2 × 10 ml), dried (K₂CO₃), and evaporated to give a mixture as a pale yellow oil (0.410 mg), which was separated by flash column chromatography. Elution with ether–light petroleum (b.p. 40–60 °C) (1 : 9) gave a mixture as a colourless oil (253 mg) and the *benzocycloheptafulranone* (20) (30 mg, 6%). The mixture was purified by flash column chromatography; elution with light petroleum (b.p. 40–60 °C) gave the *benzocycloheptafulranone* (2) as a colourless oil (211 mg, 45%) (Found: M^+ , 212.1080, C₁₅H₁₆O requires M , 212.1201); δ_{H} (C₆H₆) 1.98 (3 H, s, ArCH₃), 2.12 (3 H, s, ArCH₃), 2.72 (4 H, m, 2 CH₂), 3.57 (2 H, br, s, ArCH₂ furan), 6.05 (1 H, d, J 2 Hz, furan β -H), 6.83 (2 H, br, s, 2 ArH), and 7.03 (1 H, d, J 2 Hz, furan α -H); m/z 212 (M^+ , 92%), 197 (100), 169 (33), 149 (27), 91 (42), and 77 (25).

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