Total Synthesis of Citreomontanin, a Putative Polyene Precursor to Citreoviridin and Citreoviridinol produced by *Penicillium* sp.

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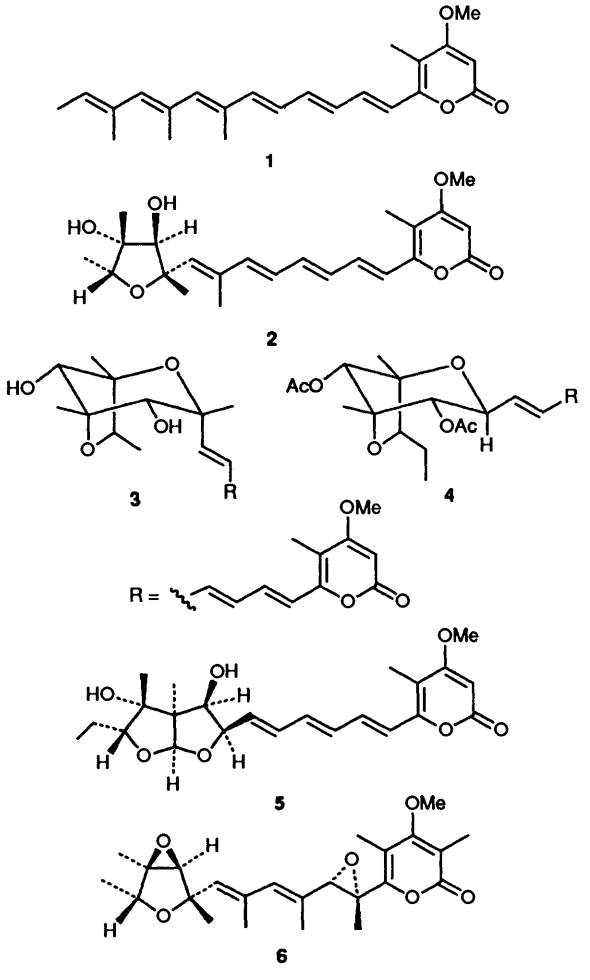
A total synthesis of all-*E*-citreomontanin, produced by *Pencillium pedemontanum* and believed to be the putative precursor of citreoviridin and citreoviridinol, involving successive epoxidations of its terminal triene portion, is described. Elaboration of the pyrone **9a** to the phosphonium salt **13b** was smoothly accomplished *via* the key pyrone aldehyde intermediates **10** and **12**. The all-*E*-trienal **7** required for Wittig coupling with compound **13b** was readily produced from the aldehyde **14** by use of two successive stereoselective Wittig olefination reactions involving the stabilised phosphorane **15**; *i.e.*, **14** + **15** ⟶ **16**, and **17** + **15** ⟶ **18**. A Wittig coupling reaction between the ylide **8** derived from **13b** and the trienal **7** then produced the all-*E*-polyene **1**, as an orange solid, which was identical with citreomontanin isolated from *P. pedemontanum*.

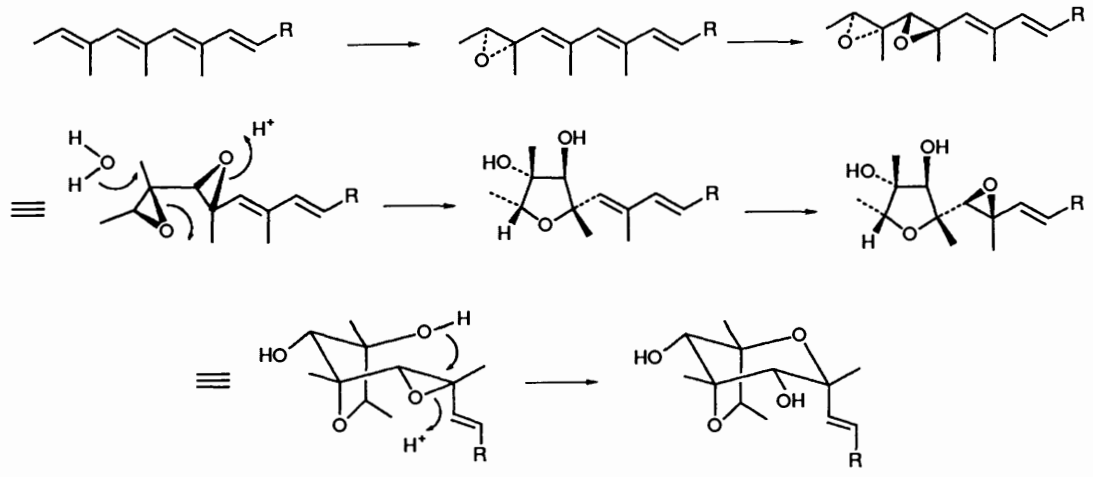
Citreomontanin **1**,[1] citreoviridin **2**[2] and citreoviridinol **3**[3] are members of a biogenetically connected family of polyene pyrone metabolites isolated from *Penicillium* sp. The molecules are also related structurally to aurovertin **4**,[4] asteltoxin **5**[5] and verrucosidin **6**[6] found in *Calcarisporium arbuscula*, *Aspergillus stellatus* and *P. verrucosum* var *cyclopium*, respectively. Citreoviridin **2** and aurovertin B **4** are potent neurotoxic mycotoxins, acting as inhibitors of ATP synthesis and hydrolysis catalysed by mitochondrial enzyme systems. The toxicity of citreoviridin, which is comparable to that of the aflatoxins, has been responsible for the occurrence of cardiac beriberi in East Asia.

It seems probable that the dioxabicyclo[3.2.1]octane ring system present in citreoviridinol **3** is derived in Nature *via* citreoviridin **2** by successive epoxidations (perhaps accompanied by 1,2-diol formation) of the trisubstituted double bonds associated with the terminal triene segment of citreomontanin **1** (see Scheme 1).[7] As a contribution to the understanding of the biogenetic interrelationships between the metabolites **1** and **3** [and also **4** and **5**], we have carried out an extensive programme of synthetic work: (i) to establish and confirm the structures and the stereochemistries assigned to these molecules, and (ii) to investigate the possible roles of epoxide intermediates in the biogenesis of the tetrahydrofuranyl and tetrahydropyranyl ring systems present in citreoviridin **2** and citreoviridinol **3** (*cf.* Scheme 1). In this paper we describe a total synthesis of citreomontanin **1** found in *P. pedemontanum*,[8a] and in the accompanying papers we outline stereocontrolled syntheses of the novel tetrahydrofuran and tetrahydropyran ring portions present in the metabolites **2**–**4**, based on the biogenetic models delineated in Scheme 1.[8b]

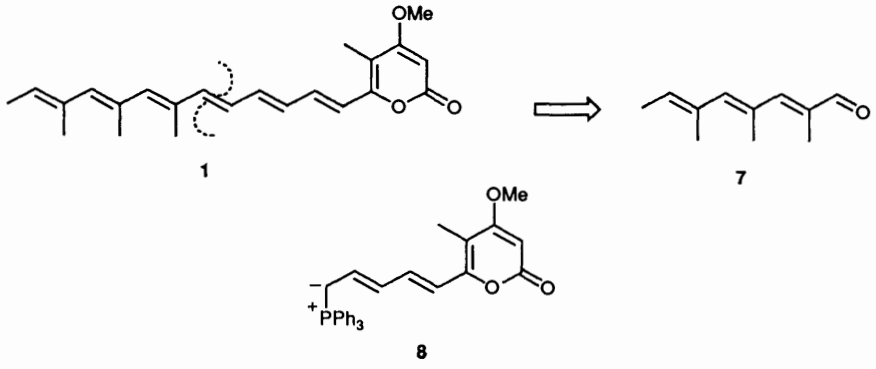
Our strategy for the synthesis of all-*E*-citreomontanin **1** relied on the development of a synthesis of the all-*E*-trienal **7**, accommodating the three trisubstituted double bonds in the natural product, followed by Wittig coupling with the phosphonium ylide **8** produced from the known 5,6-dimethyl-4-hydroxy-2-pyrone **9a** (Scheme 2).

Therefore, treatment of the pyrone **9a**[9] with dimethyl sulphate in the presence of anhydrous potassium carbonate first led to the corresponding 4-methoxypyrone **9b**. Regioselective oxidation of the C-6 methyl group in compound **9b** was then smoothly accomplished by using selenium dioxide in hot dioxane[10] to produce the 6-formylpyrone **10**, as stable yellow crystals. The structure assigned to compound **10** followed from a nuclear Overhauser difference spectrum and by analysis and comparison of its mass spectrum with literature models.[11] Condensation between the 6-formylpyrone **10** and the vinyllithium reagent produced from the vinylstannane **11**,[12] followed by *in situ* hydrolysis and dehydration of the intermediate secondary alcohol in the presence of toluene-*p*-sulphonic acid (PTSA), then gave the vinylogous all-*E*-aldehyde **12**. Reduction of compound **12** in the presence of sodium borohydride next gave rise to the allylic alcohol **13a**, which was then converted into the phosphonium salt **13b**, the precursor to ylide **8**, following bromination and treatment of the resulting bromide with triphenylphosphine.

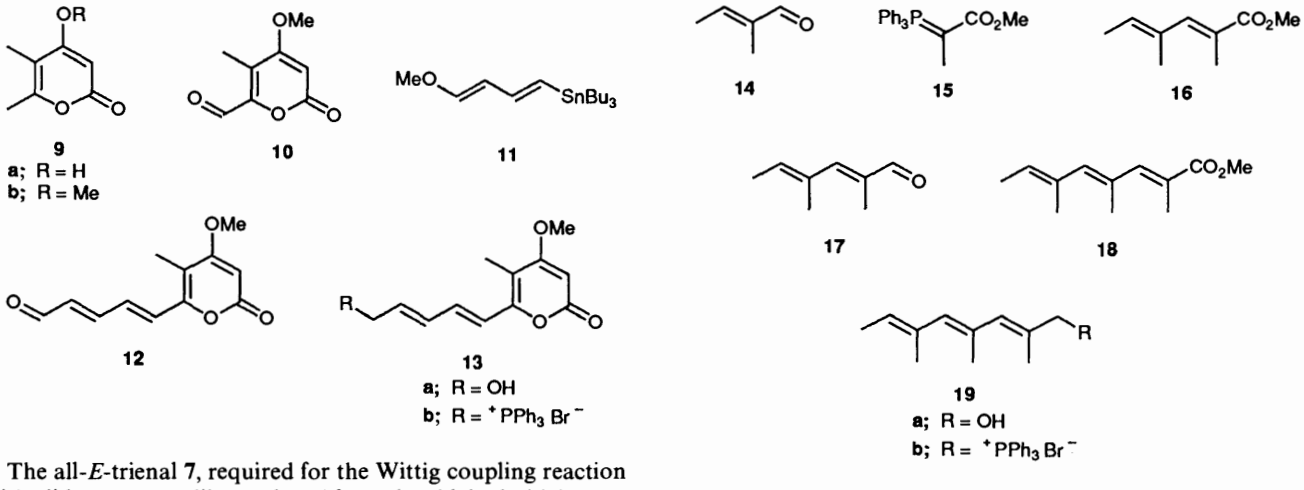




Scheme 1



Scheme 2



The all-*E*-trienal **7**, required for the Wittig coupling reaction with ylide **8**, was readily produced from the aldehyde **14**, by two stereoselective Wittig reactions involving the stabilised phosphorane **15**. Thus, condensation between aldehyde **14** and α-methoxycarbonylethylidenetriphenylphosphorane **15** in hot dichloromethane for two days, followed by work-up and distillation, first led to the *E,E*-dienoate **16**. The *E,E*-dienoate **16** was then converted into the *E,E*-dienal **17**, *via* the corresponding primary alcohol ($LiAlH_4$, then MnO_2), which, in a second stereoselective Wittig reaction with the phosphorane **15**, led to the all-*E*-trienoate **18**. Both of the polyene esters **16** and **18** were found to be homogenous in chromatographic, ^1H NMR and ^{13}C NMR analysis, and their all-*E*-stereochemistries followed conclusively from inspection and comparison (by shift data in their NMR spectra) with model compounds in the literature.[13,14]

Reduction of the trienoate **18** with lithium aluminium hydride, followed by oxidation of the resulting primary alcohol **19a**, in the presence of manganese dioxide then produced the all-*E*-trienal **7** as a liquid.

Treatment of the phosphonium salt **13b** in tetrahydrofuran (THF) with butyllithium, followed by reaction between the resulting ylide **8** and the trienal **7** at 25 °C for 2 h, then gave a mixture of the all-*E* and 11-*Z* isomers of the polyene **1** in a combined yield of 35%. Chromatography and crystallisation then provided the all-*E*-polyene **1** as an orange solid, m.p. 158–161 °C, whose ^1H NMR spectrum was superposable on that of natural citreomontanin from *P. pedemontanum*.[1,14] The all-*E*-polyene **1** was also produced, in much lower overall yields (< 10%), following a Wittig condensation between pyrone aldehyde **12** and the phosphonium salt **19b** derived from the primary alcohol **19a**.

It is interesting that, after completion of our work, Steyn and Vleggaar[15] described the outcome of their contemporaneous studies of the biosynthesis of citreoviridin **2**, using ^{13}C- and ^{18}O-isotopic labelling techniques. Their labelling studies demonstrated that the putative polyene 'starter' differs from citreomontanin in that it has a *Z*-configuration about its terminal (C-18) trisubstituted double bond.[16,*]

Experimental

M.p.s were determined on a Köfler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Pye-Unicam SP3-100 or a Philips Pu 9706 spectrometer, whereas UV spectra were recorded on a Philips Pu 8720 instrument. ^1H NMR spectra were recorded at 90 MHz on a Perkin-Elmer R 32, at 80 MHz on a Bruker WP 80 SY PFT, at 250 MHz on a Bruker WM250 PFT, or at 400 MHz on a Bruker AM 400 PFT spectrometer. ^{13}C NMR spectra were recorded on a Bruker WP 80 SY PFT, WM 250 PFT or AM 400 PFT spectrometer. Spectra were determined in deuteriochloroform solutions, unless stated otherwise, with tetramethylsilane as internal standard. *J*-Values are given in Hz. Mass spectra were recorded on an AE1 MS 902 or a VG 7070E spectrometer, and microanalyses were obtained on a Perkin-Elmer 240B elemental analyser.

Solutions involving polyenes were kept in diffuse daylight under nitrogen at all times, and were evaporated under reduced pressure at room temperature. All solutions were dried over anhydrous magnesium sulphate prior to evaporation on a Büchi rotary evaporator. Thin-layer chromatograms were run on Silica G plates, and were visualised with potassium permanganate, vanillin–sulphuric acid in ethanol, or by inspection (for polyenes).

4-Methoxy-5,6-dimethyl-2-pyrone **9b**.—A stirred mixture of 4-hydroxy-5,6-dimethyl-2-pyrone **9a**[9] (2.5 g) in dry acetone (100 cm^3), dimethyl sulphate (2.5 g) and potassium carbonate (15 g) was heated under reflux for 15 h and then cooled to room temperature. The insoluble material was removed by filtration, and then washed with acetone. The combined filtrate and washings were concentrated under reduced pressure to leave a residual oil which solidified. Recrystallisation from light petroleum (b.p. range 60–80 °C) gave *4-methoxy-5,6-dimethyl-2-pyrone* **9b** (2.32 g, 84%) as needles, m.p. 100–102 °C; λ_{max} (EtOH/nm 286; ν_{max}(KBr)/cm^{-1} 1700 and 1640; δ_H[$(CD_3)_2SO$–$CDCl_3$] 1.84 (5-Me), 2.16 (6-Me), 3.80 (OMe) and 5.40 (CH); δ_C 170.5 (C-3), 163.0 (C-2), 157.5 (C-6), 106.1 (C-5), 87.2 (C-3, d), 56.5 (OMe, q), 16.2 (6-Me, q) and 9.1 (5-Me, q) (Found: C, 62.3; H, 6.7%; M^+, 154. $C_8H_{10}O_3$ requires C, 62.3; H, 6.5%; M, 154).

4-Methoxy-5-methyl-2-oxo-2H-pyran-6-carboxaldehyde **10**.—A vigorously stirred mixture of 4-methoxy-5,6-dimethyl-2-pyrone **9b** (1 g) and selenium dioxide (3.3 g) in anhydrous 1,4-dioxane (24 cm^3) was heated under reflux for 14 h.[10] The cooled mixture was filtered, and the residue was then washed with dichloromethane–methanol (20:1). The combined filtrate and washings were evaporated to dryness under reduced pressure, and the residue was then purified by column chromatography [silica gel 50–100 mesh; CH_2Cl_2–MeOH (20:1)]. Recrystallisation from benzene gave *4-methoxy-5-methyl-2-oxo-2H-pyran-6-carboxaldehyde* **10** (0.82 g, 75%) as a yellow solid, m.p. 134–136 °C; λ_{max}($CHCl_3$)/nm 329 (infl) and 316; ν_{max}(KBr/cm^{-1} 2950, 1740, 1710 and 1610; δ_H[$(CD_3)_2SO$–$CDCl_3$] 2.24 (5-Me), 3.88 (OMe), 5.92 (=CH) and 9.80 (CHO); δ_C 183.8 (CHO, d), 168.9 (C-4), 160.7 (C-2), 148.4 (C-6), 94.2 (C-3, d), 57.3 (OMe, q) and 7.4 (5-Me, q) (Found: C, 57.0; H, 4.9%; M^+, 168.0405. $C_8H_8O_4$ requires C, 57.1; H, 4.8%; M, 168.0422).

1-Methoxy-4-(tributylstannyl)buta-1,3-diene **11**.[12]—A mixture of 1-methoxybut-1-en-3-yne (1.4 g), tributyltin hydride (5 g), and azoisobutyronitrile (50 mg) was heated at 90 °C for 16 h, and then distilled to give the stannane **12** (4.6 g, 71%) as a yellow oil, b.p. 125–135 °C at 0.5 mmHg (lit.,[12] b.p. 120–130 °C at 0.3 mmHg); ν_{max}(liq. film)/cm^{-1} 1640; δ_H 0.8–1.1 (m, 3 × Me), 1.2–1.6 (m, 9 × CH_2), 3.52 and 3.54 (OMe isomers) and 5.0–7.0 (m, 4 × CH=).

(E,E)-*5-(4-Methoxy-5-methyl-2-oxo-2H-pyran-6-yl)penta-2,4-dienal* **12**.—A solution of butyllithium in hexane (6 cm^3; 1.55 mol dm^{-3}) was added to a solution of 1-methoxy-4-tributylstannylbutadiene (3 g) in dry THF (30 cm^3) at −78 °C, and the mixture was then stirred at −78 °C for 1 h. A solution of aldehyde **11** (1 g) in dry THF (30 cm^3) was added dropwise during 0.25 h, and the mixture was stirred for 3 h. Aq. sodium hydrogen carbonate (10 cm^3) was added, and the organic product was then extracted with diethyl ether (3 × 50 cm^3). The extract was stirred with PTSA (100 mg) for 14 h, and then evaporated to dryness under reduced pressure. Column chromatography (silica; 5% MeOH–$CHCl_3$) gave the *pentadienal* **12** as an orange solid (400 mg, 28%), m.p. 185–190 °C (from MeOH); λ_{max}(EtOH)/nm 357 and 265; ν_{max}(KBr)/cm^{-1} 1710, 1680 and 1620; δ_H 2.05 (Me), 3.87 (OMe), 5.60 (pyran 3-H), 6.36 (dd, *J* 15 and 8, aldehyde 4-H), 6.82 (d, *J* 15, aldehyde 5-H), 7.17–7.38 (m, aldehyde 2- and 3-H) and 9.65 (d, *J* 8, CHO) (Found: C, 60.0; H, 5.6. $C_{12}H_{12}O_4 \cdot H_2O$ requires C, 60.5; H, 5.9%).

6-[(E,E)-*5-Hydroxypenta-1,3-dienyl*]-*4-methoxy-5-methyl-2-pyrone* **13a**.—Sodium borohydride (40 mg) was added in portions to a stirred solution of the pentadienal **12** (200 mg) in methanol (5 cm^3) dichloromethane (1 cm^3) at 25 °C. The mixture was stirred at 25 °C for 1 h and then the solvent was removed under reduced pressure. Column chromatography [silica; dichloromethane–methanol (10:1)] gave the *primary alcohol* **13a** (0.17 g, 84%) as a pale yellow solid, m.p. 170–175 °C (from MeOH); λ_{max}(EtOH/nm 344; ν_{max}(KBr)/cm^{-1} 3400 and 1710; δ_H([$^2H_4$]MeOH) 2.0 (Me), 3.92 (OMe), 4.22 (d, *J* 4, CH_2OH), 5.60 (3-H) and 6.0–7.5 (m, =CH) (Found: M^+, 222.0885. $C_{12}H_{14}O_4$ requires M, 222.0892).

(E,E)-*5-(4-Methoxy-5-methyl-2-oxo-2H-pyran-6-yl)penta-2,4-dienyl(triphenyl)phosphonium Bromide* **13b**.—A solution of the alcohol **13a** (70 mg), tetrabromomethane (115 mg) and triphenylphosphine (90 mg) in dichloromethane (15 cm^3) was stirred at 25 °C for 0.5 h. The solvent was then removed under reduced pressure to yield the crude bromide (150 mg). A solution of the crude bromide (150 mg) and triphenylphosphine (80 mg) in dichloromethane (20 cm^3) was stirred at 25 °C for 14 h. The solvent was removed under reduced pressure to leave the phosphonium salt **13b** (200 mg) as a glassy solid, which was used without further purification.

(E,E)-*Methyl 2,4-Dimethylhexa-2,4-dienoate* **16**.—A solution of the aldehyde **14** (3.8 g) and 1-(methoxycarbonyl)ethylidene-(triphenyl)phosphorane **15**[18] (16 g) in dichloromethane (200 cm^3) was heated under reflux under nitrogen for 48 h. The mixture was evaporated to dryness under reduced pressure to leave a residue, which was then triturated under light petroleum (b.p. range 40–60 °C). The precipitated triphenylphosphine oxide was filtered off, and the filtrate was then evaporated to leave an oil, which was distilled to give the *dienoate* **16** (4.9 g,

* Citreomontanin **1** has not been detected in *Penicillium pedemontanum* IFO 9583, from which citreoviridinols, *e.g.* **3**, have recently been isolated.[17]

73%) as a liquid, b.p. 54 °C at 0.1 mmHg; λ_{max}(EtOH)/nm 266; ν_{max}(liq. film)/cm^{-1} 1720 and 1620; δ_H 1.76 (d, *J* 7, *Me*CH=), 1.86 (4-Me), 2.04 (2-Me), 3.80 (CO_2Me), 5.76 (q, *J* 7, MeC*H*=) and 7.12 (=CH); δ_C 169.8, 143.3 (d), 130.9 (d), 133.1, 124.7, 51.8 (q), 16.0 (q) and 14.0 (q) (Found: M$^+$, 154.0982. $C_9H_{14}O_2$ requires M, 154.0993), which was homogeneous by GLC (OV 17; 170 °C).

(E,E)-(2,4-*Dimethylhexa*-2,4-*dien*-1-*ol*.—A solution of (*E,E*)-methyl 2,4-dimethyl hexa-2,4-dienoate (4.9 g) in dry diethyl ether (25 cm^3) was added dropwise to a stirred slurry of lithium aluminium hydride (1.2 g) in dry diethyl ether (50 cm^3), at such a rate as to maintain gentle reflux. The mixture was heated under reflux for 12 h and then cooled to 5 °C. Ethyl acetate (1 cm^3) was added dropwise, followed by water (5 cm^3), and the mixture was then acidified with dil. sulphuric acid and extracted with diethyl ether (4 × 50 cm^3). The extracts were washed with saturated aq. sodium hydrogen carbonate, then dried, and evaporated under reduced pressure. Distillation of the residue gave the title alcohol (4 g, 85%) as a liquid, b.p. 48–50 °C at 0.05 mmHg; λ_{max}(EtOH)/nm 231; ν_{max}(liq. film)/cm^{-1} 3350, 1460 and 1030; δ_H 1.6 (OH) (disappears on D_2O shake), 1.65–1.85 (m, 3 × Me), 4.02 (CH_2), 5.42 (q, *J* 7, MeC*H*=) and 5.90 (=CH) (Found: M$^+$, 126.1044. $C_8H_{14}O$ requires M, 126.1045).

(E,E)-2,4-*Dimethylhexa*-2,4-*dienal* **17**.—A solution of (*E,E*)-2,4-dimethylhexa-2,4-dien-1-ol (20.3 g) in dichloromethane (1500 cm^3) was stirred at room temperature in the presence of manganese dioxide (200 g), until chromatographic analysis showed that all the starting material had been consumed. The mixture was filtered, and the residue was washed with dichloromethane. Evaporation of the filtrate left the *aldehyde* **17** (13.5 g, 68%) as an oil, λ_{max}(EtOH)/nm 280; ν_{max}(liq. film)/cm^{-1} 2900, 1700 and 1630; δ_H 1.6–2.1 (3 × Me), 6.04 (q, *J* 8, MeC*H*=), 6.78 (=CH) and 9.4 (CHO), which was used without further purification. The 2,4-*dinitrophenylhydrazone derivative* was crystallised from ethanol, and had m.p. 174–176 °C (Found: C, 53.7; H, 5.4; N, 17.8%; M$^+$, 304.1165. $C_{14}H_{16}N_4O_4 \cdot 0.5H_2O$ requires C, 53.7; H, 5.4; N, 17.9%; $C_{14}H_{16}N_4O_4$ requires M, 304.1171).

(E,E,E)-*Methyl* 2,4,6-*Trimethylocta*-2,4,6-*trienoate* **18**.—From the general procedure described for the preparation of compound **16**, reaction between the aldehyde **17** (0.1 g) and methoxycarbonylethylidene(triphenyl)phosphorane **15**[18] (0.3 g) gave the *all*-E-*trienoate* **18** (60 mg, 40%) as a liquid, b.p. 80 °C at 0.07 mmHg (Kugelrohr oven); λ_{max}(EtOH/nm 296; ν_{max}(liq. film)/cm^{-1} 1720 and 1620; δ_H 1.5–2.2 (m, 4 × Me), 3.78 (CO_2Me), 5.55 (q, *J* 8, MeC*H*=), 6.06 (5-H) and 7.20 (3-H); δ_C 13.9 (q), 14.1 (q), 16.5 (q), 18.2 (q), 51.8 (q), 125.3, 127.0 (d), 130.9, 133.3, 139.0 (d), 144.4 (d) and 169.7 (Found: M$^+$, 194.1313. $C_{12}H_{18}O_2$ requires M, 194.1307), which was homogeneous by GLC (OV 17; 180 °C).

(E,E,E)-2,4,6-*Trimethylocta*-2,4,6-*trien*-1-*ol* **19a**.—By the general procedure described above, reduction of (*E,E,E*)-methyl 2,4,6-trimethylocta-2,4,6-trienoate **18** (1.9 g) with lithium aluminium hydride (360 mg) gave the *triene alcohol* **19a** (1.3 g, 82%) as a liquid, b.p. 60–62 °C at 0.05 mmHg; ν_{max}(film)/cm^{-1} 3300 and 1450; δ_H 1.50–2.0 (m, 4 × Me), 2.1 (OH), 4.06 (CH_2), 5.45 (q, *J* 8), 5.84 (5-H) and 5.96 (3-H) (Found: M$^+$, 166.1356. $C_{11}H_{18}O$ requires M, 166.1358).

(E,E,E)-2,4,6-*Trimethylocta*-2,4,6-*trienal* **7**.—By the general procedure, described for the preparation of aldehyde **17**, reaction between 2,4,6-trimethylocta-2,4,6-trien-1-ol **19a** (0.5 g) and manganese dioxide (5 g) gave the trienal **7** (0.3 g, 61%) as a liquid; λ_{max}(EtOH)/nm 282; ν_{max}(liq. film)/cm^{-1} 2970, 2930, 1690 and 1630; δ_H 1.7–1.9 (m, 4-, 6- and 7-Me), 2.14 (2-Me), 5.68 (q, *J* 8, MeC*H*), 6.30 (5-H), 6.80 (3-H) and 9.45 (CHO). The 2,4-*dinitrophenylhydrazone derivative* was crystallised from ethanol, and had m.p. 157–158 °C (Found: C, 59.2; H, 6.0; N, 16.5%; M$^+$, 344.1464. $C_{17}H_{20}N_4O_4$ requires C, 59.3; H, 5.8; N, 16.3%; M, 344.1466).

(E,E,E)-2,4,6-*Trimethylocta*-2,4,6-*trienyl*(*triphenyl*)*phosphonium Bromide* **19b**.—A solution of (*E,E,E*)-2,4,6-trimethylocta-2,4,6-trien-1-ol **19a** (0.25 g) and triphenylphosphine hydrobromide (0.53 g) in dry methanol (5 cm^3) was stirred at 25 °C for 6 days under nitrogen. The solvent was removed under reduced pressure, and the oily residue was then triturated under diethyl ether and dried to leave a glassy solid (0.78 g, 100%), which was used without further purification.

4-*Methoxy*-5-*methyl*-6-[(*all*-E)-7,9,11-*trimethyltrideca*-1,3,5,7,9,11-*hexaenyl*]-2-*pyrone* (*Citreomontanin*) **1**.—(*a*) A solution of sodium methoxide (1 cm^3) [prepared from sodium (30 mg) in dry methanol (10 cm^3) was added dropwise to a stirred solution of (*E,E,E*)-2,4,6-trimethylocta-2,4,6-trienyl(triphenyl)phosphonium bromide **19b** (150 mg) and 5-(4-methoxy-5-methyl-2-oxo-2*H*-pyran-6-yl)penta-2,4-dienal **12** (30 mg) in dry dimethylformamide (10 cm^3) at 25 °C under nitrogen. The mixture was stirred for 3 h at 25 °C, then brine (20 cm^3) was added, and the aq. layer was extracted with diethyl ether. The combined extracts were concentrated under reduced pressure to leave a brown oil, which after repeated chromatography [silica; hexane–acetone (2:1)] gave the polyene **1** (1 mg, 2%) identical with that described under *b*.

(*b*) A solution of butyllithium in hexane (0.2 cm^3; 1.54 mol dm^{-3}) was added to a suspension of the phosphonium bromide **13b** (0.2 g) in dry THF (10 cm^3) under nitrogen, and the mixture was then stirred at room temperature for 10 min. A solution of (*E,E,E*)-2,4,6-trimethylocta-2,4,6-trienal **19a** (50 mg) in dry THF (5 cm^3) was added, and the mixture was then stirred for 2 h at 25 °C. The solvent was removed under reduced pressure and the oily residue was then extracted with diethyl ether. The combined extracts were concentrated under reduced pressure to leave a brown oil, which was purified by column chromatography (Kieselgel G; diethyl ether). Crystallisation from diethyl ether gave citreomontanin **1** (17 mg, 16%) as an orange solid, m.p. 135–145 °C (Köfler), 158–161 °C (sealed tube, *in vacuo*) (natural citreomontanin has m.p. 165–166 °C);[1] λ_{max}(EtOH)/nm 416 (29 600); ν_{max}(KBr)/cm^{-1} 1710, 1630, 1540, 1410 and 1250; δ_H 1.73 (3 H, d, *J* 7, *Me*CH=), 1.79, 1.97 and 1.98 (12 H, 3 × s, 4 × Me), 3.80 (3 H, OMe), 5.50 (1 H, 3-H), 5.50 (q, *J* 7, MeC*H*), 5.90 (1 H, 10′-*H*), 6.10 (1 H, 8′-*H*), 6.2–6.8 (6 H, m, [CH=CH]$_3$) and 7.25 (1 H, dd, *J* 10 and 14, 2′-H) (Found: M$^+$, 352.2028. Calc. for $C_{23}H_{28}O_3$: M, 352.2038).

Acknowledgements

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