

Capnellane Sesquiterpenes. Total Synthesis of Epiprecapnelladiene and $\Delta^{8(9)}$ -Capnellene

Alan M. Birch and Gerald Pattenden*
 Department of Chemistry, The University, Nottingham NG7 2RD

The total synthesis of epiprecapnelladiene(29) containing an uncommon bicyclo[6.3.0]undecane carbon skeleton is described. The fused 5,8-ring system in (29) is elaborated in a single step, using a highly regio- and stereo-selective intramolecular photocycloaddition reaction from the enol benzoate(16a). The relative stereochemistry of precapnelladiene, from the soft coral *Capnella imbricata*, is established as that in formula (30).

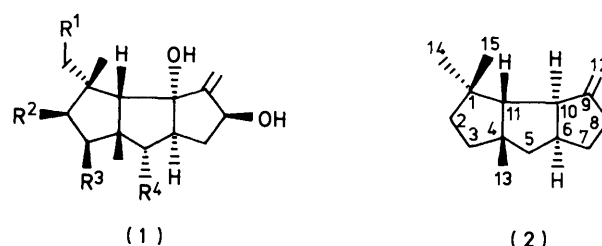
In a biogenetically patterned synthesis, treatment of epiprecapnelladiene(29) or its *exo*-methylene isomer(28), with boron trifluoride-diethyl ether is shown to lead to $\Delta^{8(9)}$ -capnellene(32), accompanied by smaller amounts of the positional isomers (33) and (34).

Capnellane is the generic name applied to the family of sesquiterpene alcohols (1a–e) and the hydrocarbon (2), found in the soft coral *Capnella imbricata*.^{1,2} The family is characterised by the presence of a tricyclo[6.3.0.0^{2,6}]undecane ring system, which is also found in the hirsutane group of sesquiterpenes, represented by hirsutic acid (3), hirsutene (4), and coriolin (5).³ The hydrocarbon (2), $\Delta^{9(12)}$ -capnellene, is the presumed biosynthetic precursor of the capnellensols (1). Although the biosynthetic origin of (2) has not been established, it is almost certain that like the hirsutane carbon framework it derives ultimately from humulene by a series of transannular reactions involving a fused 5,8-membered carbocyclic system as a key intermediate.⁴ Compelling support for this proposal came with the isolation, in 1979, of a second sesquiterpene hydrocarbon from *C. imbricata* which was isomeric with (2) and given the novel structure (6);⁵ the molecule was designated 'precapnelladiene'. In this paper we describe the total synthesis of epiprecapnelladiene,[†] and its transannular cyclisation to the capnellane carbon framework, which provides support for some of the biosynthetic speculation mentioned above.⁶

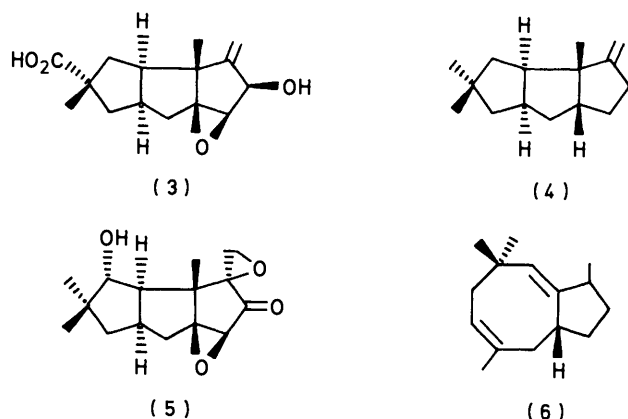
Precapnelladiene(6) has an uncommon fused 5- and 8-membered ring system, hitherto found only in a few sester- and di-terpenoids *e.g.* ophiobolans (7)⁷ and fusicoccins (8),⁸ and in the related molecules poitediol (9)⁹ and dactylol (10)¹⁰ isolated from marine organisms. In spite of numerous investigations,¹¹ the synthesis of natural terpenes incorporating this novel fusion of 5- and 8-rings, until this study, has not previously been accomplished.

In the previous paper,¹² we described a novel approach to the fused 5,8-ring system present in precapnelladiene, which was based on regioselective intramolecular photocycloaddition of the pentenyl substituted enol ester (11), to (12), followed by retro-aldolisation to (13). This approach seemed particularly appropriate for the synthesis of the corresponding trimethyl substituted cyclo-octane-1,5-dione (22) which we hoped to elaborate to precapnelladiene (6).

Alkylation of the anion (14) obtained from 2,4-dimethoxycyclohexa-1,4-diene,¹³ with 5-iodohex-1-ene first led to the substituted bis-ether (15) which on hydrolysis followed by benzylation gave the enol benzoate (16a). Irradiation of a solution of the enol benzoate (16a) in hexane through Pyrex using a 450-W medium-pressure lamp then gave, in both a regio- and stereo-selective manner, the photoadduct (18), in *ca.* 98% isolated yield. The stereochemistry assigned to the adduct (18) followed from *X*-ray analysis of the crystalline



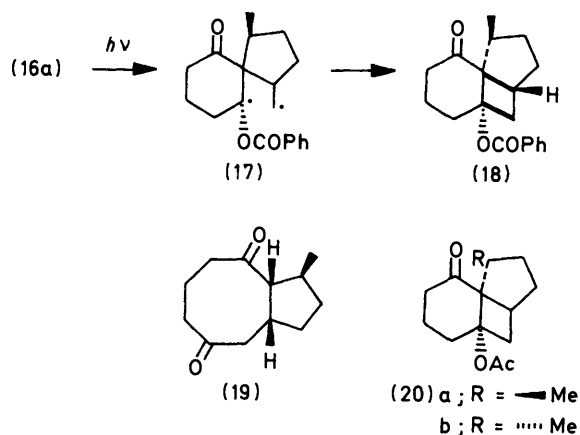
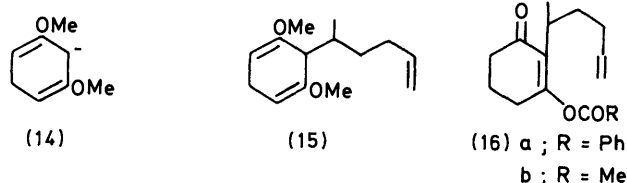
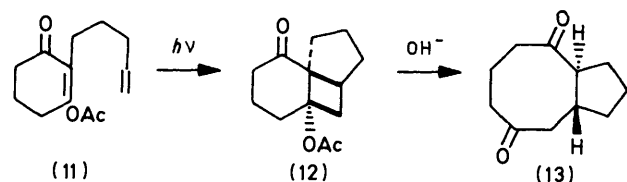
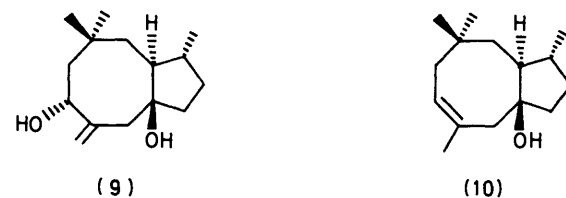
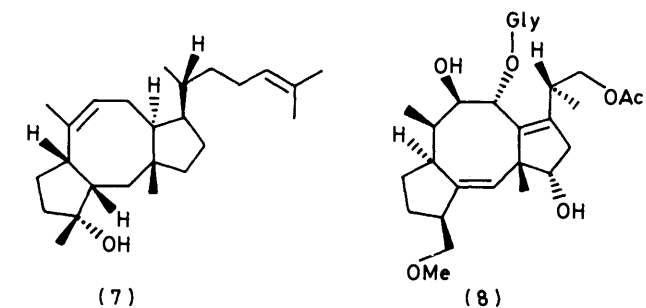
- (1)
 a ; R¹ = R² = R³ = H, R⁴ = OH
 b ; R¹ = R² = R⁴ = H, R³ = OH
 c ; R¹ = R³ = R⁴ = H, R² = OH
 d ; R¹ = R³ = H, R² = R⁴ = OH
 e ; R² = R⁴ = H, R¹ = R³ = OH



dione(19) produced after saponification-retro-aldolisation in ethanolic potassium hydroxide.‡ The *X*-ray data established a *cis*-fusion of the two rings in the dione (19) [*cf.* structure (13)]¹² with the 5-ring methyl group on the same β -face of the molecule as the *cis*-angular hydrogen atoms. The *anti*-relationship of the benzoate and methyl groups in the photo-adduct (18) follows from a biradical mechanism for the intramolecular cycloaddition involving the spirocyclic diradical species (17) as intermediate (see discussion in ref. 12). Molecular models clearly reflect strong steric interactions between the benzoate and methyl groups in (17) when they are *syn*- to one another. Interestingly, irradiation of the corresponding enol acetate

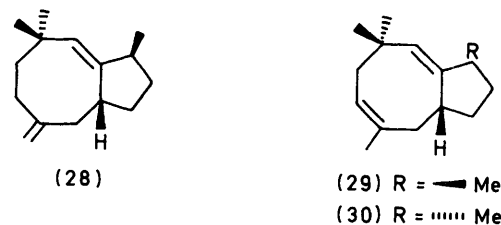
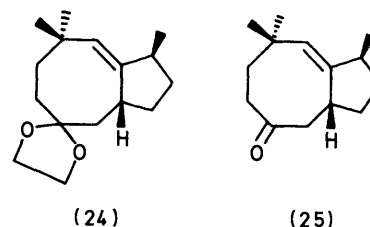
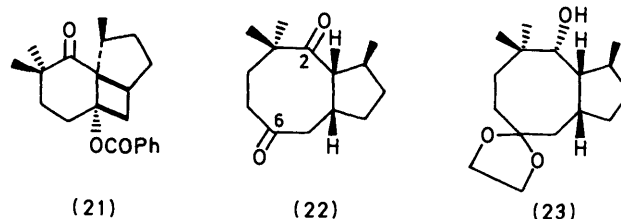
† Structural investigations did not establish the relative stereochemistry of natural precapnelladiene.

‡ We thank Dr. M. J. Begley of this department for this information which will be published separately.



(16b) derived from (15) was found to be less selective, with upwards of 8% of the methyl epimer (20b) of the adduct (20a) being produced concurrently.

Treatment of the keto-benzoate (18) with lithium hexamethyldisilazide, followed by methyl iodide, led to the *gem*-dimethyl substituted adduct (21) which on fragmentation in base then gave the trimethyl substituted cyclo-octane-1,5-dione (22). The bridgehead double bond in precapnelladiene was next introduced following selective protection of the C-6 carbonyl group in (22) as the corresponding dioxolane, reduction with lithium aluminium hydride to the *anti*-carbinol (23),

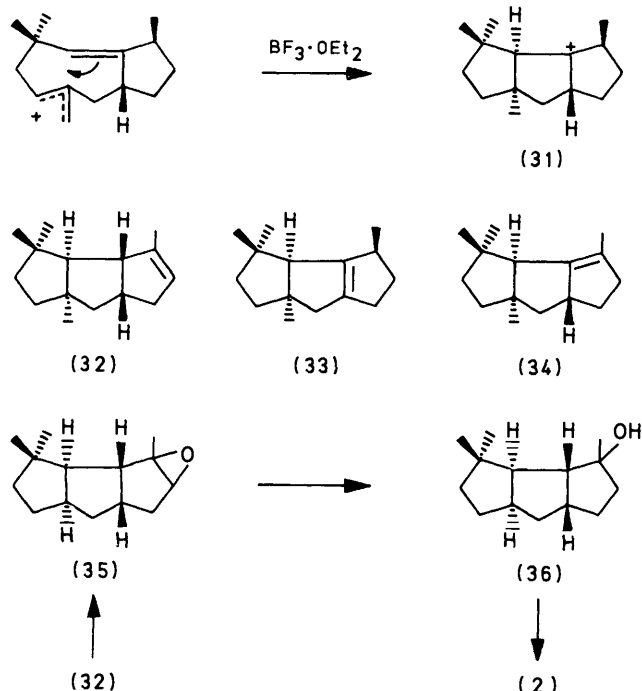


dehydration of (23) to (24) using phosphorus trichloride oxide in pyridine,¹⁴ and finally regeneration of the carbonyl in (24), leading to the enone (25).

We had intended to introduce the trisubstituted double bond at C(5)-C(6) in precapnelladiene by methylation of the vinyl anion (26) derived from the trisylhydrazone derivative of the ketone (25) (*i.e.* Shapiro reaction).¹⁵ Although we were able to form the vinyl anion (26), our attempts to quench the intermediate with methyl iodide were unsuccessful; in all cases we instead isolated norprecapnelladiene (27) produced from rapid *in situ* quenching of the anion (26) by a proton source within the reaction medium. The desired trisubstituted double bond was ultimately introduced in a highly regioselective manner by prior conversion into the *exo*-methylene compound (28), using the Wittig reaction, and isomerisation of the exocyclic double bond in (28) with rhodium trichloride in refluxing ethanol.¹⁶

Although the i.r. and mass spectral data of our synthetic precapnelladiene were identical with those of the naturally derived material, small chemical-shift differences between the 2-H (δ 4.92 synthetic; 5.06 natural) and 11-Me (δ 0.99 synthetic; 1.03 natural) resonances in their ¹H n.m.r. spectra showed that the molecules were indeed epimeric at C-11. Since our synthesis had led to the *syn*-diastereoisomer (29), these data establish the relative stereochemistry of natural precapnelladiene as in formula (30).

Treatment of our epiprecapnelladiene (29) with boron trifluoride-diethyl ether in benzene under reflux for 1 h resulted in clean transannular cyclisation to one major new hydro-



carbon (>50%) accompanied by two minor isomeric hydrocarbon products.¹⁷ The major product was separated and purified by chromatography on silica gel impregnated with silver nitrate. It showed n.m.r. spectral data [δ_{H} 1.67(CMe) and 5.13(CH); δ_{C} 122.0(d), and 143.1 p.p.m.] expected for $\Delta^{8(9)}$ -capnellene (32), and the *cis*-, *anti*-, *cis*-stereochemistry followed from comparison of proton and carbon n.m.r. shift data with those reported for natural $\Delta^{9(12)}$ -capnellene (2). The minor hydrocarbon products obtained from transannular cyclisation of epiprecapnelladiene were not completely resolved by chromatography, but spectral data on partly separated materials (>75% resolved), established that they were the $\Delta^{6(10)}$ -[δ 0.83 (Me), 0.97 (d, *J* 7, CHMe), 1.02 (Me), and 1.15 (Me)] and $\Delta^{9(10)}$ -[δ 0.81 (Me), 1.09 (Me), 1.17 (Me), and 1.61 (CMe)] isomers, (33) and (34) respectively, of (32). Although the *exo*-methylene isomer (28) led to the same mixture of hydrocarbons (32), (33), and (34), we were unable to detect the presence of natural $\Delta^{9(12)}$ -capnellene (2) in any of the mixtures resulting from treatment of (28) or (29) with boron trifluoride.

It seems likely that the isomeric capnellenes (32), (33), and (34) result from the same carbocation intermediate (31) produced from transannular cyclisation of (28) or (29), and that the major [$\Delta^{8(9)}$]capnellene product (32) arises as a consequence of isomerisation (*in situ*, and partly during chromatography) of the bridgehead [$\Delta^{9(10)}$]capnellene (34).

After the completion of our studies, Matsumoto *et al.*¹⁸ described an alternative multi-step preparation of the hydrocarbon (32) starting from humulene 6,7-epoxide. The same authors also converted the hydrocarbon (32) into natural $\Delta^{9(12)}$ -capnellene (2) *via* the tertiary alcohol (36) derived from the corresponding epoxide (35).*

Experimental

For general experimental details see previous papers.^{12,20}

2,4-Dimethoxy-3-(1-methylpent-5-enyl)cyclohexa-1,4-diene (15).—Freshly prepared 2,4-dimethoxycyclohexa-1,4-diene (3.96 g)¹³ was added to a solution of *t*-butyl-lithium (1.6M in pentane; 21 ml) in dry tetrahydrofuran (160 ml) at -70°C under nitrogen, and the mixture was then stirred at -70°C for 1 h. The stirred mixture was treated with dry hexamethylphosphoramide (5.8 ml) followed, after 0.25 h, by 5-iodohex-1-ene²¹ (7.8 g) whereupon the orange-brown solution was almost completely decolourised. The mixture was allowed to warm to room temperature when it was diluted with saturated aqueous sodium chloride (100 ml) and extracted with *n*-pentane (2×100 ml). The pentane extracts were then washed with water (50 ml) and saturated aqueous sodium chloride (50 ml), dried, and evaporated. Distillation of the residue gave the substituted cyclohexadiene (4.6 g, 74%) as a colourless liquid, b.p. $100\text{--}102^\circ\text{C}$ at 1 mmHg, v_{max} (film) 1 684, 1 215, 1 205, and 1 145 cm^{-1} ; δ 0.82 (d, *J* 7, CHMe), 1.1–2.2 (m, 5 H) 2.74 (m, 3 H), 3.47 ($2 \times$ OMe), 4.6 (m, 2 H), 4.76–4.95 (m, 2 H), and 5.4–5.9 (m, 1 H) (Found: M^+ , m/z 222.1627. $\text{C}_{14}\text{H}_{22}\text{O}_2$ requires M , 222.1620).

1-Acetoxy-2-(1-methylpent-5-enyl)cyclohex-1-en-3-one (16b).—1M-Hydrochloric acid (27 ml) was added to a solution of 2,4-dimethoxy-3-(1-methylpent-5-enyl)cyclohexa-1,4-diene (4 g) in acetone (80 ml), which had been previously purged with nitrogen, and the mixture was then left at 25°C for 1 h before being evaporated almost to dryness under reduced pressure. The residue was diluted with brine (70 ml), and then extracted with methylene dichloride. After being washed with water, the methylene dichloride extracts were dried, and then evaporated to leave crude (1-methylpent-5-enyl)cyclohexane-1,3-dione as a beige, waxy solid. A solution of the 1,3-dione in acetic anhydride (66 ml) containing anhydrous sodium acetate (0.66 g) was stirred at 25°C for 24 h and then evaporated under reduced pressure. The residue was diluted with water (150 ml) and then extracted with ether (4×125 ml). Evaporation of the washed (saturated NaHCO_3) and dried ether extracts left the acetate which was purified by chromatography on silica using ether–light petroleum (b.p. $40\text{--}60^\circ\text{C}$) (1 : 1) as eluant. The acetate (2.6 g, 61%) had b.p. $106\text{--}110^\circ\text{C}$ at 1 mmHg, v_{max} (film) 1 760, 1 675, 1 645, and 1 200 cm^{-1} ; δ 1.07 (d, *J* 6, CHMe), 1.35–2.8 (m, 11 H), 2.18 (OAc), 4.74–4.9 (m, 2 H), and 5.3–5.8 (m, 1 H) (Found: M^+ , m/z 236.1427. $\text{C}_{14}\text{H}_{26}\text{O}_3$ requires M , 236.1412).

1-Benzoyloxy-2-(1-methylpent-5-enyl)cyclohex-1-en-3-one (16a).—A solution of (1-methylpent-5-enyl)cyclohexane-1,3-dione [prepared from 2,4-dimethoxy-3-(1-methylpent-5-enyl)cyclohexa-1,4-diene (4.45 g), as described above] in pyridine (15 ml) at 0°C was treated with benzoyl chloride (3.3 g) and the mixture was stirred at 25°C for 3 days; it was then poured into hydrochloric acid (1M; 200 ml) and extracted with ether (3×100 ml). The combined ether extracts were washed with dilute hydrochloric acid (50 ml) and brine (50 ml) and then dried and evaporated. Purification of the residue by chromatography on silica in methylene dichloride gave the benzoate (4.5 g, 76%) as a colourless oil, v_{max} (film) 1 730, 1 665, 1 255, 1 230, 1 100, and 700 cm^{-1} ; δ 1.1 (d, *J* 7, CHMe), 1.3–3.3 (m, 11 H) 4.72–4.95 (m, 2 H), 5.4–5.9 (m, 1 H), 7.32–7.64 (m, 3 H), and 7.9–8.06 (m, 2 H) (m/z 298.1581. $\text{C}_{15}\text{H}_{22}\text{O}_3$ requires M , 298.1569) homogeneous in g.l.c. (10% SE-30; 230°C).

6-Benzoyloxy-11-methyltricyclo[6.3.0.0^{1,6}]undecan-2-one (18).—A solution of 1-benzoyloxy-2-(1-methylpent-5-enyl)cyclohex-1-en-3-one (4.46 g) in hexane (2 l) was purged with nitrogen for 0.25 h, and then irradiated through Pyrex using a 450-W medium-pressure Hg lamp. The progress of the reaction was monitored using g.l.c. (10% SE-30, 230°C) and

* Two other syntheses of $\Delta^{9(12)}$ -capnellene were reported during the course of our studies.

was stopped when g.l.c. analysis showed that all the starting material had been consumed (*ca.* 6 h). Evaporation of the hexane left the tricyclic keto-ester (4.35 g) as a colourless oil, v_{\max} 1 720, 1 690, 1 450, 1 105, and 710 cm^{-1} ; δ 0.8—2.92 (m, 14 H), 1.03 (d, *J* 7.5, CHMe), 7.38—7.68 (m, 3 H), and 7.9—8.2 (m, 2 H) (Found: M^+ , m/z 298.1581. $\text{C}_{15}\text{H}_{22}\text{O}_3$ requires *M*, 298.1569), which was homogeneous by g.l.c.

Irradiation of the corresponding enol acetate (16b), under similar conditions, led to one major cycloadduct (>90%) accompanied by a minor product of longer retention time in g.l.c. analysis. The mixture of photoproducts gave the dione (19) on treatment with ethanolic potassium hydroxide, thereby suggesting that it was composed of a mixture of the methyl epimers (20a) (major) [δ 0.89 (CHMe)] and (20b) (minor) [δ 0.86 (CHMe)].

cis-9-Methylbicyclo[6.3.0]undecane-3,7-dione (19).—A solution of 6-benzoyloxy-11-methyltricyclo[6.3.0.0^{1,6}]undecan-2-one (0.14 g) and potassium hydroxide (0.2 g) in ethanol (15 ml) was stirred at 25 °C for 48 h and then poured into water (50 ml) and extracted with pentane (10 ml) followed by ether (3 × 10 ml). The combined extracts were washed with water (3 × 10 ml) and brine (10 ml), and then dried and evaporated. Chromatography of the residue on silica using ether–light petroleum (b.p. 40—60 °C) (1 : 1) as eluant gave the dione (0.03 g) which crystallised from ether as thin plates, m.p. 66—67 °C, v_{\max} 1 705, 1 695, 1 450, and 1 220 cm^{-1} ; δ 0.98 (d, *J* 7, CHMe) and 1.1—3.0 (m, 15 H) (Found: C, 74.0; H, 9.2%; M^+ , m/z 194.1313. $\text{C}_{12}\text{H}_{18}\text{O}_2$ requires C, 74.2; H, 9.3%, *M*, 194.1306).

6-Benzoyloxy-3,3,11-trimethylbicyclo[6.3.0.0^{1,6}]undecan-2-one (21).—A solution of 6-benzoyloxy-11-methyltricyclo[6.3.0.0^{1,6}]undecan-2-one (0.5 g) in dry tetrahydrofuran (10 ml) was added dropwise over 10 min to a stirred solution of lithium hexamethyldisilazide [from BuⁿLi(1.3M; 5.16 ml) in hexane and hexamethyldisilazane (1.09 g)] in dry tetrahydrofuran (30 ml) at –70 °C. The mixture was stirred at –70 °C for 0.25 h and then treated with methyl iodide (1 g) over 10 min. After being allowed to warm to 25 °C, the mixture was stirred at this temperature for 3.5 h, and then poured into water (150 ml) and extracted with ether (2 × 100 ml). The ether extracts were washed with water (50 ml) and saturated ammonium chloride solution (2 × 50 ml), and then dried and evaporated to leave the crude bis-methylated ketone (0.55 g). A sample was purified by chromatography on silica using ether–light petroleum (b.p. 40—60 °C) as eluant, and showed v_{\max} 1 720, 1 690, 1 285, 1 110, and 720 cm^{-1} ; δ 0.99 (d, *J* 7.5, CHMe), 1.11 (Me), 1.15 (Me), 1.2—3.96 (m, 12 H), 7.3—7.6 (m, 3 H), and 7.9—8.1 (m, 2 H); the chromatographic purification resulted in considerable losses of material.

cis-3,3,11-Trimethylbicyclo[6.3.0]undecane-2,6-dione (22).—A solution of the crude (>95% by g.l.c. analysis; SE-30, 240 °C) 6-benzoyloxy-3,3,11-trimethylbicyclo[6.3.0.0^{1,6}]undecan-2-one (0.5 g) in dimethyl sulphoxide (30 ml) and aqueous potassium hydroxide (5 ml; 20% v/v) was kept at 25 °C for 12 h; it was then poured into water (100 ml), and the pH of the mixture adjusted to pH 8. The mixture was extracted with ether–light petroleum (b.p. 40—60 °C) (2 : 1) (3 × 50 ml), and the combined extracts were then washed with water (3 × 50 ml), dried, and evaporated. Chromatography of the residue on silica using benzene–ether (1 : 1) as eluant then gave the solid dione (0.11 g, 36%), which crystallised from light petroleum (b.p. 40—60 °C) as colourless microcrystals, m.p. 77.5—78.5 °C, v_{\max} (CHCl₃) 1 705, 1 685, 1 460, and 1 370 cm^{-1} ; δ 0.93 (d, *J* 7.5, CHMe), 1.14 (2 × Me), 1.2—2.7 (m, 12 H), and 2.9 (dd, *J* 8.5 and 7.5, CHCO) (Found: C, 75.5; H,

10.3%; *M*, 222.1324. $\text{C}_{14}\text{H}_{22}\text{O}_2$ requires C, 75.6; H, 10.0%; *M*, 222.1620).

3-Ethylenedioxy-6,6,9-trimethylbicyclo[6.3.0]undecan-7-ol (23).—A solution of 3,3,11-trimethylbicyclo[6.3.0]undecane 2,6-dione (0.46 g) in benzene (20 ml) containing ethylene glycol (0.14 g) and toluene-*p*-sulphonic acid (1 mg) was heated under reflux using a Dean and Stark trap for 6 h. The solution was cooled, and then washed with 2M-sodium hydroxide solution (2 × 10 ml) and brine (10 ml), and dried. Evaporation of the solution left 3-ethylenedioxy-6,6,9-trimethylbicyclo[6.3.0]undecane (0.53 g, 98%) as a colourless oil, v_{\max} 1 695, 1 445, and 1 100 cm^{-1} ; δ 0.95 (d, *J* 7, CHMe), 1.03 (Me), 1.13 (Me), 1.2—2.75 (m, 12 H), 2.98 (dd, *J* 9.5 and 8.5; CHCO), and 3.86 (4 H) (Found: M^+ , m/z 266.1887. $\text{C}_{16}\text{H}_{26}\text{O}_3$ requires *M*, 266.1882), which was found to be homogeneous by g.l.c. (SE-30, 200 °C).

Lithium aluminium hydride (35 mg) was added to a solution of the above acetal (0.1 g) in dry ether (10 ml), and the solution then heated under reflux for 4 h. The mixture was cooled, and then treated dropwise with water (0.5 ml). The ether extracts were separated and washed with brine (10 ml) and then dried. Evaporation of the ether left the carbinol (0.089 g, 89%) as a colourless oil, v_{\max} 3 500, 1 450, 1 120, and 1 080 cm^{-1} ; δ 0.92 (Me), 1.0 (d, *J* 7, CHMe), 1.02 (Me), 1.2—2.2 (m, 13 H), 2.7—3.0 (m, 1 H), 3.28br (1 H), and 3.9 (m, 4 H) (Found: M^+ , m/z 268.2047. $\text{C}_{16}\text{H}_{28}\text{O}_3$ requires *M*, 268.2038).

6-Ethylenedioxy-3,3,11-trimethylbicyclo[6.3.0]undec-1-ene (24).—A solution of 3-ethylenedioxy-6,6,9-trimethylbicyclo[6.3.0]undecan-7-ol (0.32 g) in dry pyridine (7 ml) and phosphorus trichloride oxide (0.5 ml) was left at 25 °C for 10 days, and then poured into water (75 ml) and extracted with ether (3 × 40 ml). The combined ether extracts were diluted with light petroleum (b.p. 40—60 °C) (40 ml) and then washed with water (4 × 20 ml) and brine (40 ml), and dried. Evaporation of the solvents, and chromatography of the residue on silica using benzene–ether (4 : 1) as eluant gave the alkene (0.23 g, 76%) as a colourless oil, v_{\max} 1 610, 1 460, and 1 110 cm^{-1} ; δ 0.98 (2 × Me), 1.0 (d, *J* 7, CHMe), 1.1—2.5 (m, 11 H), 3.02br (1 H), 3.96 (4 H), 4.87 br (:CH) (Found: M^+ , m/z 250. $\text{C}_{10}\text{H}_{26}\text{O}_2$ requires *M*, 250) which was homogeneous in g.l.c. (SE-30, 200 °C).

3,3,11-Trimethylbicyclo[6.3.0]undec-1-en-6-one (25).—A solution of 6-ethylenedioxy-3,3,11-trimethylbicyclo[6.3.0]undec-1-ene (0.34 g) in tetrahydrofuran (0.75 ml), water (0.75 ml), and acetic acid (2.25 ml) was kept at 25 °C for 12 h, and then diluted with water (50 ml) and extracted with ether (3 × 30 ml). The separated ether extracts were washed successively with 1M-sodium hydroxide solution (30 ml), water (30 ml), and brine (30 ml), and then dried. Evaporation of the ether left the enone (0.28 g, 99%) as a colourless oil, v_{\max} 1 700, 1 460, 1 380, and 1 360 cm^{-1} ; δ 0.96 (d, *J* 7, CHMe), 1.1 (2 × Me), 1.2—2.7 (m, 10 H), 2.8—3.0 (m, 1 H), 3.6br (1 H), and 5.02br (:CH) (Found: M^+ , m/z 206.1687. $\text{C}_{14}\text{H}_{22}\text{O}$ requires *M*, 206.1671).

3,3,11-Trimethylbicyclo[6.3.0]undeca-1,5-diene (27).—A solution of 3,3,11-trimethylbicyclo[6.3.0]undec-1-en-6-one (0.1 g) and trisylhydrazine (0.15 g) in methanol containing hydrochloric acid (0.5 ml of a solution prepared from 2 drops of conc. HCl in 8 ml MeOH), was kept at 0.2 °C for 15 h. The precipitated hydrazone (0.1 g, 40%) was filtered off, washed with cold methanol, and dried *in vacuo*. *n*-Butyllithium (4 equiv.) in hexane (0.5 ml) was added to a vigorously stirred suspension of the trisylhydrazone (0.1 g) in

hexane (4.5 ml) containing tetramethylethylenediamine (0.5 ml) at -70°C . The mixture was kept at -70°C for 0.3 h, and then allowed to warm to 0°C when it was treated with freshly distilled methyl iodide (0.15 g). The mixture was stirred at 25°C for 0.5 h and then diluted with water (50 ml) and extracted with light petroleum (b.p. $40-60^{\circ}\text{C}$) (3×10 ml). The light petroleum extracts were washed with water (2×10 ml) and brine (10 ml), and then dried and evaporated under reduced pressure. Chromatography of the residue on silica using light petroleum (b.p. $40-60^{\circ}\text{C}$) as eluant gave the 1,5-diene (51 mg) as an oil, δ 1.05 (d, *J* 6, *CHMe*), 1.1 ($2 \times$ Me), 1.6–2.1 (m, 5 H), 2.2–3.2 (m, 4 H), 3.6 (m, 1 H), 5.1 (m, :CH), and 6.2–6.8 (m, *CH:CH*) [Found: M^+ , m/z 190, 136(100) ($-C_4H_6$). $C_{14}H_{22}$ requires *M*, 190], homogeneous in g.l.c. (SE-30, 200°C).

3,3,11-Trimethyl-6-methylenebicyclo[6.3.0]undec-1-ene (28).—A solution of 3,3,11-trimethylbicyclo[6.3.0]undec-1-en-6-one (0.18 g) in dry tetrahydrofuran (2 ml) was added over 5 min to a stirred solution of methylenetriphenylphosphoranyl-ide [from methyltriphenylphosphonium bromide (1.6 g) and Bu^nLi (1.9M; 2.3 ml)] in tetrahydrofuran (10 ml), and the mixture was then stirred at 25°C for 16 h. The mixture was poured into water (60 ml) and extracted with ether (3×30 ml); the combined ether extracts were then washed with water (30 ml) and brine (30 ml), dried, and evaporated. Chromatography of the residue on silica (50–100 mesh) using light petroleum (b.p. $40-60^{\circ}\text{C}$) as eluant gave the diene (0.16 g, 86%) as a colourless oil, ν_{max} . 3 070, 1 640, 1 460, 1 380, 1 360, 890, and 870 cm^{-1} ; δ 0.97 (Me), 1.06 (d, *J* 7, *CHMe*), 1.08 (Me), 1.1–2.6 (m, 11 H), 3.4br (1 H), 4.57br (1 H), 4.75br (1 H), and 4.97br (1 H) (Found: M^+ , m/z 204.1885. $C_{15}H_{24}$ requires *M*, 204.1878), which was homogeneous in g.l.c. (SE-30, 190°C).

3,3,6,11-Tetramethylbicyclo[6.3.0]undeca-1,5-diene (Epiprecapnelladiene) (29).—A solution of 3,3,11-trimethyl-6-methylenebicyclo[6.3.0]undec-1-ene (50 mg) in ethanol (12 ml) was heated under reflux in the presence of rhodium chloride trihydrate (62 mg) for 0.75 h; the mixture was then cooled and poured into aqueous potassium cyanide (40 ml; 2.5%) and extracted with light petroleum (b.p. $40-60^{\circ}\text{C}$) (2×20 ml). The combined extracts were washed with water (20 ml) and brine (20 ml), and then dried and evaporated. Chromatography of the residue on silica using light petroleum (b.p. $40-60^{\circ}\text{C}$) as eluant gave the isomerised diene (25 mg, 50%) as a colourless oil, ν_{max} . 1 460, 1 380, 1 360, 865, and 855 cm^{-1} ; δ 0.98 ($2 \times$ Me), 0.99 (d, *J* 6.7, *CHMe*), 1.65 (:CMe), 1.74–2.03 (m, 5 H), 2.25–2.45 (m, 3 H), 2.93 (dd, *J* 13 and 9, *CH:CH'*), 3.55br (1 H), 4.92 (m, :CH), 5.36br (t, *J* ca. 9, :CH:CH₂); δ_c 19.6(q), 26.7(q), 29.6(q), 31.8, 32.6, 37.9, 38.5, 39.0, 39.9, 43.8(t), 121.8(d), 136.6, and 145.8 p.p.m. (Found: M^+ , m/z 204.1854. $C_{15}H_{24}$ requires *M*, 204.1878), which was homogeneous in g.l.c. (SE-30, 190°C).

$\Delta^{8(9)}$ -Capnellene (32).—A solution of epiprecapnelladiene (25 mg) in dry benzene (5 ml) was heated in the presence of boron trifluoride-ether (5 drops) for 1 h, and then cooled and poured into saturated aqueous sodium hydrogen carbonate (10 ml). The mixture was extracted with ether (2×15 ml), and the separated ether extracts were then washed with brine (10 ml) and dried. Evaporation of the ether left a residue (ca. 18 mg) which showed three peaks in g.l.c. analysis (SE-30, 160°C) present in the approximate ratio 3 : 2 : 5. Chromatography on silica impregnated with 15% silver nitrate using light petroleum (b.p. $30-40^{\circ}\text{C}$) as eluant gave the following. (i) $\Delta^{8(9)}$ -Capnellene (8.4 mg) (eluted last), homogeneous in t.l.c. and g.l.c. and showing: δ 0.94(Me), 1.03(Me),

1.1(Me), 1.67(:CMe), and 5.13(:CH); δ_c 15.1(q), 25.6(q), 29.7(t), 30.7(q), 31.3(q), 39.4(t), 40.3(t), 41.8, 43.6(d), 51.0(t), 52.8, 56.9(d), 64.6(d), 122.0(d), and 143.1 p.p.m. (Found: M^+ , m/z 204.1884. $C_{15}H_{24}$ requires *M*, 204.1878). (ii) $\Delta^{6(10)}$ -Capnellene (33) (ca. 2 mg) (eluted first), >72% pure by g.l.c. analysis [δ 0.83(Me), 0.97(d, *J* 7, *CHMe*), and 1.15(Me)]. (iii) $\Delta^{9(10)}$ -Capnellene (34) (ca. 2 mg) (eluted second), 75% pure by g.l.c. analysis [δ 0.81(Me), 1.09(Me), 1.17(Me), and 1.61 (:CMe)].

The same ratio of capnellenes was produced when the *exo*-methylene isomer(28) of epiprecapnelladiene was treated in a similar manner with boron trifluoride-ether.

Acknowledgements

We thank Professor Djerassi for providing spectra of naturally derived precapnelladiene and $\Delta^{9(12)}$ -capnellene. We also thank the S.E.R.C. for a fellowship (to A. M. B.) and the Royal Society for an equipment grant.

References

- 1 Y. M. Sheikh, G. Singy, M. Kaisin, H. Eggert, C. Djerassi, B. Tursch, D. Daloz, and J. C. Braekman, *Tetrahedron*, 1976, **32**, 1171.
- 2 E. Ayanoglu, T. Gebreyesus, C. M. Beechan, C. Djerassi, and M. Kaisin, *Tetrahedron Lett.*, 1978, 1671.
- 3 See: F. W. Comer, F. McCapra, I. H. Qureshi, and A. I. Scott, *Tetrahedron*, 1967, **23**, 4761; T. Kunimoto, M. Hori, and H. Umezawa, *Biochem. Biophys. Acta*, 1973, **298**, 513; P. G. Mantle and G. Mellows, *Trans. Br. Mycol. Soc.*, 1973, **61**, 513.
- 4 For bibliography and relevant recent work see: K. Hayano, Y. Ohfuné, H. Shirahama, and T. Matsumoto, *Helv. Chim. Acta*, 1981, **64**, 1347; Y. Murata, T. Ohtsuka, H. Shirahama, and T. Matsumoto, *Tetrahedron Lett.*, 1981, **22**, 4313.
- 5 E. Ayanoglu, T. Gebreyesus, C. M. Beechan, and C. Djerassi, *Tetrahedron*, 1979, **35**, 1035.
- 6 Preliminary communications: A. M. Birch and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 1980, 1195; *Tetrahedron Lett.*, 1982, **23**, 991.
- 7 G. A. Cardell, *Phytochemistry*, 1974, **13**, 2343; J. S. Calderon, L. Quijano, and T. Rios, *Chem. Ind. (London)*, 1978, 584.
- 8 K. D. Barrow, D. H. R. Barton, E. B. Chain, U. F. W. Ohnsorge, and R. P. Sharma, *J. Chem. Soc., Perkin Trans. I*, 1973, 1590.
- 9 W. Fenical, G. R. Schulte, J. Finer, and J. Clardy, *J. Org. Chem.*, 1978, **43**, 3628.
- 10 F. J. Schmitz, K. H. Hollenbeak, and D. J. Vanderah, *Tetrahedron*, 1978, **34**, 2719.
- 11 See T. K. Das, P. C. Dutta, G. Kartha, and J. M. Bernassan, *J. Chem. Soc., Perkin Trans. I*, 1977, 1287; W. G. Dauben and D. J. Hart, *J. Org. Chem.*, 1977, **42**, 922; R. K. Boeckmann, J. P. Bershas, J. Clardy, and B. Solheim, *ibid.*, 1977, **42**, 3630.
- 12 M. J. Begley, M. Mellor, and G. Pattenden, *J. Chem. Soc., Perkin Trans. I*, 1983, preceding paper.
- 13 A. J. Birch, *J. Chem. Soc.*, 1947, 102; A. J. Birch and H. Smith, *ibid.*, 1951, 1882; E. Piers and J. R. Grierson, *J. Org. Chem.*, 1977, **42**, 3755.
- 14 Cf. W. S. Allen and S. Bernstein, *J. Am. Chem. Soc.*, 1955, **77**, 1028.
- 15 See: R. H. Shapiro, *Organic Reactions*, 1976, **23**, 405.
- 16 Cf. R. E. Rinehart and J. S. Lasky, *J. Am. Chem. Soc.*, 1964, **86**, 2516; E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3178.
- 17 For examples of the synthesis of bicyclo-octanes by transannular reactions involving cyclo-octa-1,5-dienes see: L. Paquette, *Fortschr. Chem. Forsch.*, 1979, **79**, 43.
- 18 T. Fujita, T. Ohtsuka, H. Shirahama, and T. Matsumoto, *Tetrahedron Lett.*, 1982, 4091.
- 19 (a) R. D. Little and G. L. Carroll, *Tetrahedron Lett.*, 1981, **22**, 4389; (b) K. E. Stevens and L. A. Paquette, *ibid.*, 1981, **22**, 4393.
- 20 A. J. Barker and G. Pattenden, *J. Chem. Soc., Perkin Trans. I*, 1983, 1885.
- 21 N. O. Brace, *J. Org. Chem.*, 1967, **32**, 2711.