Synthesis Based on Cyclohexadienes. Part 9.[1] Total Synthesis of (±)-Seychellene

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A new strategy for the total synthesis of (±)-seychellene 1 is described. The key step is an intramolecular Michael addition involving a 6-exo cyclisation with a vinyl radical derived from the acetylenic compound 11, obtained from the bicyclo[2.2.2]octene adduct 5 to the tricyclic intermediates 14 and 15.

The sesquiterpene, seychellene 1 was isolated as a minor constituent[2] from the essential oil of Patchouli, distilled from the leaves of *Pogostemon cablin* Benth. The structure and its absolute configuration was established[3] as 3β,6α,8α-trimethyl-2-methylenetricyclo[5.3.1.0^{3,8}]undecane from chemical degradation studies. A number of syntheses of compound 1 have been reported[4-12] since it has a unique molecular architecture. We describe a new strategy for the stereospecific synthesis of seychellene from methyl 5-*endo*-acetyl-3,4-dimethylbicyclo-[2.2.2]oct-2-ene-2-carboxylate 3.[13] Preliminary results of this investigation have been reported.[14]

Our synthetic strategy was to carry out an intramolecular radical-initiated Michael addition of the allyl bromide 2, readily available from the adduct 3, to build the tricyclic framework of seychellene 1 as depicted in Scheme 1.

3 R = Me
5 R = H

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7

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Scheme 1
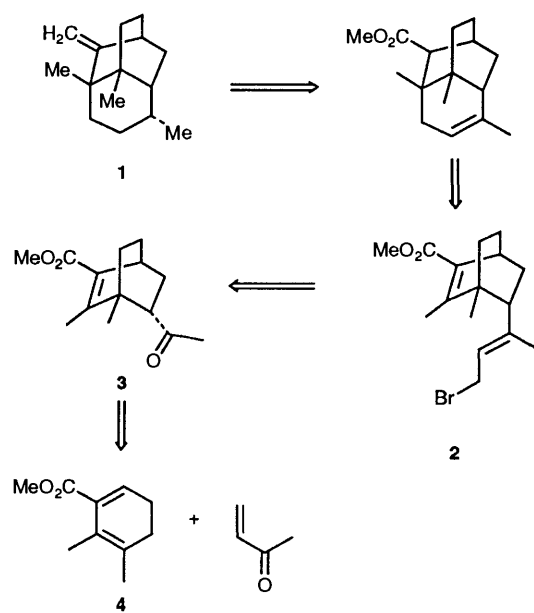
The bicyclic adduct 3 was obtained[1] by the cycloaddition of the diene ester 4 with methyl vinyl ketone. Hydrolysis of ester 3 with methanolic potassium hydroxide gave the acid 5, which was treated with vinylmagnesium bromide in tetrahydrofuran (THF), followed by esterification with ethereal diazomethane to give the alcohol 6 in good yield. Reaction of the tertiary alcohol 6 with PBr$_3$ in methylene dichloride afforded the rearranged primary bromide 2, which was subjected to an intramolecular radical cyclisation to obtain the desired tricyclic system.

Reaction of the bromide 2 with a 0.02 mol dm^{-3} solution of tributyltin hydride (TBTH) in benzene in the presence of azoisobutyronitrile (AIBN) afforded exclusively the ester 7,
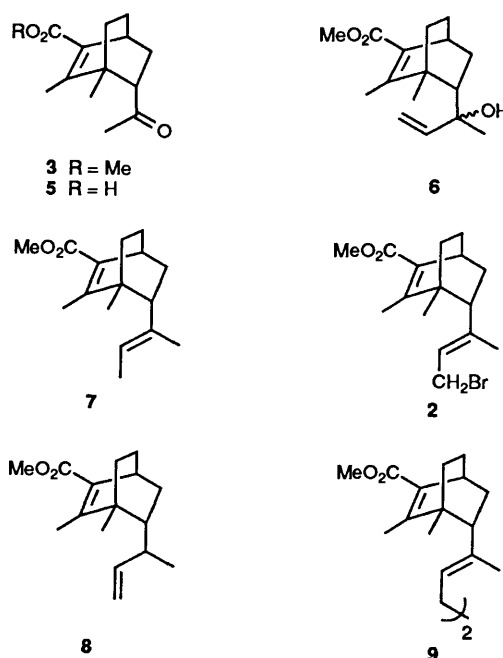
wherein reduction rather than cyclisation had occurred. Reaction of bromide 2, with TBTH under dilute conditions (0.002 mol dm^{-3} solution) resulted in a mixture of products 8 and 9 in a 3:2 ratio. The formation of these two products clearly indicated that the initially formed allyl radical is either isomerised or dimerised and did not participate in the intramolecular Michael reaction although such bond formations have been reported elsewhere.[15,16] The failure of the allyl radical to form the required carbon–carbon bond is perhaps due to its steric rigidity. Reaction of the bromide 2 with zinc[17] in THF yielded the dimeric product 9. Since intramolecular Michael reaction of an allyl radical failed to result in the required tricyclic system an alternative method involving a vinyl radical was investigated in an attempt to obtain the desired tricyclic system. Vinyl radicals can be readily generated[18] from acetylenes and hence compound 11 was chosen for the above transformation.

Reaction of the acid 5 with prop-2-ynylmagnesium bromide yielded the alcohol acid 10. The acetylenic ester 11, prepared from acid 10 with ethereal diazomethane, on reaction with TBTH afforded the tricyclic stannane 12 in 75% yield. Chromatographic purification of compound 12 on silica gel resulted in the demetallated compound 13 (5%) besides the stannane 12 (95%). (Protiodestannylation on silica gel is known.[18]) The structures of these compounds were deduced from their ^{1}H NMR spectral data; in particular the ^{1}H NMR

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10 R = H
11 R = Me

12 R = SnBu$_3$
13 R = H

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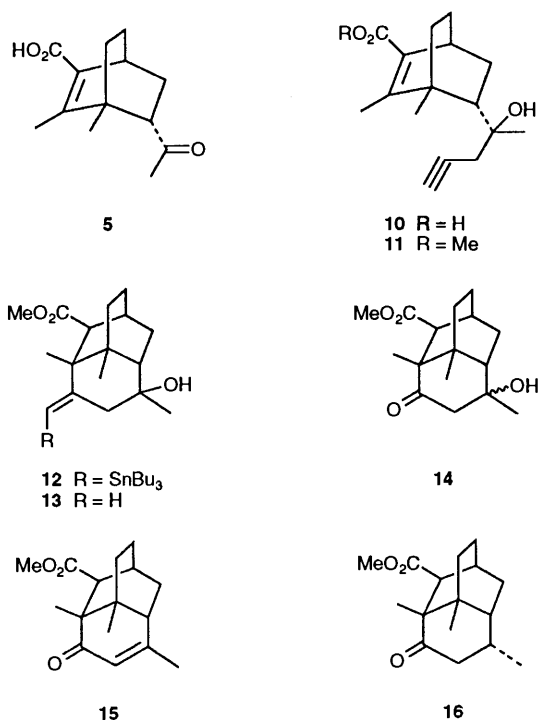
spectrum of compound **12** showed the presence of three singlets at δ 1.28, 1.25 and 0.76 for the three methyl groups, besides other resonances confirming that the vinyl radical participated in the intramolecular Michael reaction resulting in the tricyclic product **13** arising out of 6-*exo* cyclisation. The stannane derivative **12**, obtained from alkynol **11** by radical cyclisation, is a single isomer as judged from its ^{1}H NMR spectrum and hence the double bond in compound **12** appears to have *E* stereochemistry, although this could not be substantiated.

Oxidation of the stannane **12** with ruthenium trichloride[19] in the presence of sodium metaperiodate afforded the hydroxy ketone **14**. Treatment of compound **14** in benzene with toluene-*p*-sulfonic acid (PTSA) adsorbed on silica gel[20] resulted in the keto compound **15**, which was hydrogenated in the presence of 10% Pd–C to afford exclusively the keto ester **16** having an equatorial methyl group. This had been expected since the hydrogenation can take place only from the less hindered β-face. Direct reduction of the keto group in compound **16** under Wolf–Kishner conditions or though the formation of the thioketal followed by hydrogenolysis resulted in a complex mixture of products and hence an alternative method for the conversion of the keto ester **16** into the ester **19** was devised.

Reduction of the keto ester **16** with sodium borohydride in

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19 R = CO$_2$Me
20 R = CH$_2$OH

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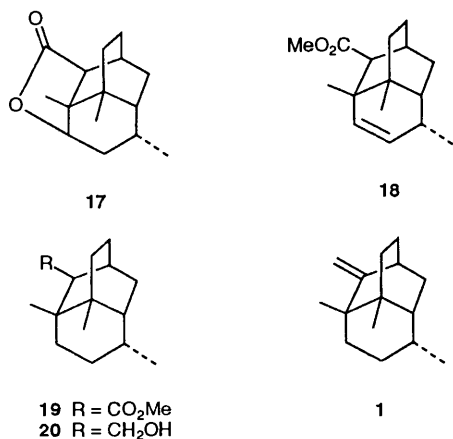
ethanol afforded the γ-lactone **17**, identical with the product obtained by the oxidation[3] of seychellene, thus confirming the structure and stereochemistry of the tetracyclic lactone **17**. Refluxing of the lactone **17** with thionyl dichloride[21] in methanol yielded the unsaturated ester **18**, which was hydrogenated to the saturated ester **19**. Reduction (LiAlH$_4$) of the ester **19** gave the alcohol **20** which, on dehydration[22] with methanesulfonyl chloride, triethylamine, and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) in refluxing toluene afforded (±)-seychellene **1** in good yield. The identity of the synthetic (±)-alcohol **20** and of (±)-seychellene **1** was established by spectral comparison with the authentic specimens, kindly provided by Prof. G. Ourisson.

In conclusion, an efficient method for the construction of a carbon–carbon bond involving a 6-*exo* cyclisation of a vinyl radical, an intramolecular Michael reaction, is described. This was exemplified by the total synthesis of (±)-seychellene from a bicyclo[2.2.2]octane derivative.

Experimental

M.p.s were measured on a Mettler FPI apparatus and are un-corrected. IR spectra were recorded as liquid films or Nujol mulls on a Perkin-Elmer model 781 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer for solutions in CDCl$_3$ unless otherwise stated. Chemical shifts are reported in δ-units with SiMe$_4$ as internal standard, and *J*-values are in Hz. Mass spectra were determined on a JEOL MS-DMX 303 spectrometer with a built-in direct-inlet system. Microanalyses were carried out using a Carlo Erba 1106 instrument. Analytical TLC was performed on glass plates coated with Acme's silica gel G (with 13% calcium sulfate as the binder). Work-up usually involved dilution of the reaction mixture with water, extraction with diethyl ether, washing of the extract successively with water, brine and water, followed by drying (Na$_2$SO$_4$), and evaporation under reduced pressure. The residue was purified by chromatography on silica gel and the product was eluted with hexane containing ethyl acetate (5%).

5-endo-Acetyl-3,4-dimethylbicyclo[2.2.2]oct-2-ene-2-carboxylic Acid **5**.—A mixture of methyl 5-*endo*-acetyl-3,4-dimethyl-bicyclo[2.2.2]oct-2-ene-2-carboxylate **3** (2.36 g, 10 mmol) and KOH (2 g) in methanol (20 cm^3) was stirred at room temperature for 12 h. After removal of methanol, the residue was diluted with water (100 cm^3) and acidified with 10% HCl. The mixture was extracted with diethyl ether and worked up to afford the *keto acid* **5** (2.1 g, 95%), which was crystallised from methanol, m.p. 132–133 °C; ν_{max}/cm^{-1} 3300–2500, 1710, 1665 and 1605; δ_H 12.2 (1 H, br s, CO$_2$H), 3.4–3.2 (1 H, m, bridgehead H), 2.61 (1 H, dd, *J* 10 and 6, CHCO), 2.25 (3 H, s, Me), 2.35–1.1 (6 H, m, 3 × CH$_2$), 1.98 (3 H, s, Ac) and 1.19 (3 H, s, Me) (Found: C, 70.3; H, 8.1. C$_{13}$H$_{18}$O$_3$ requires C, 70.2; and H, 8.2%).

Methyl 5-(1-Hydroxy-1-methylprop-2-enyl)-3,4-dimethylbi-cyclo[2.2.2]oct-2-ene-2-carboxylate **6**.—A solution of vinyl bromide (0.57 cm^3, 8 mmol) in dry THF (10 cm^3) was added to a mixture of magnesium (200 mg, 8 mmol) and iodine in dry THF (10 cm^3). After initiation of the reaction, the mixture was cooled to 0 °C and the halide was added dropwise under nitrogen with stirring of the mixture until all the magnesium had dissolved. This reagent was added dropwise to a stirred solution of the keto acid **5** (0.6 g, 2.7 mmol) in dry THF (10 cm^3) at 0 °C and the mixture was stirred for a further 12 h before being decomposed with aq. NH$_4$Cl and worked up to give a viscous material, which was esterified with ethereal diazometh-ane. The crude ester was purified to yield the *allyl alcohol* **6**

(0.46 g, 65%); v_{max}/cm^{-1} 3500, 1710, 1620, 1280, 1260 and 920; δ_H 6.03–4.73 (3 H, m, CH_2=CH), 3.63 (3 H, s, COOMe), 3.16–2.93 (1 H, m, bridgehead H), 2.06 (3 H, s, Me), 2.0–0.8 (8 H, m), 1.33 (3 H, s, Me) and 1.0 (3 H, s, Me) (Found: C, 72.6; H, 9.2. $C_{16}H_{24}O_3$ requires C, 72.69 and H, 9.15%).

Methyl 5-(3-Bromo-1-methylprop-1-enyl)-3,4-dimethylbicyclo[2.2.2]oct-2-ene-2-carboxylate **2**.—A solution of PBr_3 (0.3 cm^3, 3 mmol) in dry methylene dichloride (5 cm^3) was added dropwise to a stirred solution of the allyl alcohol **6** (0.4 g, 1.5 mmol) in dry methylene dichloride (10 cm^3) at 0 °C. The mixture was stirred for 12 h and on work-up gave the allyl bromide **2** (0.38 g, 77%); v_{max}/cm^{-1} 1710, 1645, 1615, 1255, 1220 and 1060; δ_H 5.43 (1 H, t, J 8, olefinic), 3.86 (2 H, d, J 8, CH_2Br), 3.66 (3 H, s, OMe), 3.26–3.0 (1 H, m, bridgehead H), 2.33–0.83 (7 H, m), 2.06 (3 H, s, Me), 1.46 (3 H, s, Me) and 1.0 (3 H, s, Me).

Methyl 3,4-Dimethyl-5-(1-methylprop-1-enyl)bicyclo[2.2.2]-oct-2-ene-2-carboxylate **7**.—A solution of the allyl bromide **2** (100 mg) in benzene (35 cm^3) was treated with TBTH (0.11 cm^3, 1.25 mol equiv.) and AIBN (cat.) at 80 °C for 4 h. Removal of the solvent followed by the usual work-up gave the *title product* **7** (70 mg, 72%), v_{max}/cm^{-1} 1710, 1615, 1255 and 1220; δ_H 5.1 (1 H, q, =CH), 3.6 (3 H, s, CO_2Me), 3.23–3.0 (1 H, m, bridgehead H), 2.3–0.8 (7 H, m), 2.06 (3 H, s, Me), 1.5 (3 H, d, J 8, Me), 1.3 (3 H, br s, Me) and 1.0 (3 H, s, Me) (Found: C, 77.4; H, 9.7. $C_{16}H_{24}O_2$ requires C, 77.37; H, 9.74%).

Dimer **9**.—A mixture of bromide **2** (100 mg), dry THF (35 cm^3) and zinc wool (20 mg) was refluxed for 4 h and then quenched with saturated aq. NH_4Cl. The product **9** (66 mg, 88%) was obtained after the usual work-up, v_{max}/cm^{-1} 1710, 1615, 1255 and 1220; δ_H 5.0 (2 H, t, 2 × =CH), 3.6 (6 H, s, 2 × CO_2Me), 3.23–3.0 (2 H, m, bridgehead H), 2.26–0.8 (18 H, m), 2.06 (6 H, s, 2 × Me), 1.3 (6 H, s, 2 × Me) and 0.96 (6 H, s, 2 × Me); m/z M$^+$, 494 and 435 (M$^+$ − CO_2Me).

Methyl 5-(1-Hydroxy-1-methylbut-3-ynyl)-3,4-dimethylbicyclo[2.2.2]oct-2-ene-2-carboxylate **11**.—A solution of prop-2-ynyl bromide (2.4 cm^3, 27 mmol) in dry THF (50 cm^3) was added to a mixture of magnesium (0.65 g, 27 mmol), mercury(II) chloride (5 mg) and iodine. After initiation of the reaction, the mixture was cooled to 0 °C, the addition of halide was continued dropwise under nitrogen, and the reaction mixture was stirred until all the metal had dissolved. This reagent was added dropwise to a stirred solution of the keto acid **5** (1.2 g, 5.45 mmol) in dry THF (100 cm^3) at 0 °C and the mixture was stirred for 12 h. After decomposition with 5% aq. HCl, the organic layer was worked up. The product, after esterification with ethereal diazomethane, gave the *ester* **11** (1.4 g, 94%) as a pale yellow liquid, v_{max}/cm^{-1} 3500, 3300, 2100, 1690 and 1610; δ_H 3.73 (3 H, s, CO_2Me), 3.14 (1 H, s, bridgehead H), 2.3–1.75 (6 H, m), 2.2 (3 H, s, Me), 1.6–0.8 (5 H, m), 1.38 (3 H, s, Me) and 0.95 (3 H, s, Me) (Found: M$^+$, 276.1724; C, 73.8; H, 8.7. $C_{17}H_{24}O_3$ requires M, 276.1725; C, 73.9 and H, 8.7%).

Methyl 6-Hydroxy-3,6,8-trimethyl-4-(tributylstannylmethylene)tricyclo[5.3.1.0³·⁸]undecane-2-carboxylate **12** *and Methyl 6-Hydroxy-3,6,8-trimethyl-4-methylenetricyclo[5.3.1.0³·⁸]undecane-2-carboxylate* **13**.—A solution of the ester **11** (1.38 g, 5 mmol) in benzene (500 cm^3) was treated with TBTH (1.68 cm^3, 1.25 mol equiv.) and AIBN (cat.) at 80 °C for 24 h. Usual work-up afforded a mixture (2.13 g, 75%), which was separated by chromatography on silica gel. Elution with ethyl acetate–hexane (1:19) afforded compound **12** (2.02 g, 95%); v_{max}/cm^{-1} 3600–3300, 1730 and 1580; δ_H 5.67 (1 H, s, =CH), 3.53 (3 H, s, CO_2Me), 2.7 (1 H, J 14), 2.35 (1 H, s, CH), 1.99 (1 H, s, bridgehead H), 1.97 (1 H, J 14), 1.73–1.26 (8 H, m), 1.28 (3 H,

s, Me), 1.25 (3 H, s, Me), 0.93–0.86 (27 H, m, Bu_3) and 0.76 (3 H, s, Me).

Further elution, with ethyl acetate–hexane (1:9), afforded compound **13** (5%); v_{max}/cm^{-1} 3500, 1730 and 1630; δ_H 4.97 (1 H, s, vinylic), 4.88 (1 H, s, vinylic), 3.57 (3 H, s, CO_2Me), 1.99–1.93 (3 H, m), 1.89–1.23 (7 H, m), 1.29 (3 H, s, Me), 1.19 (3 H, s, Me) and 0.94 (3 H, s, Me) (Found: M$^+$, 278.1884. Calc. for $C_{17}H_{26}O_3$: 278.1882).

Methyl 6-Hydroxy-3,6,8-trimethyl-4-oxotricyclo[5.3.1.0³·⁸]-undecane-2-carboxylate **14**.—Ruthenium trichloride (5 mg) was added to a mixture of the stannane **12** (0.57 g, 1 mmol) in a mixture of carbon tetrachloride (2 cm^3), acetonitrile (2 cm^3), water (3 cm^3) and sodium metaperiodate (877 mg, 4.1 mol equiv.) and the reaction mixture was stirred vigorously at room temperature for 6 h. It was then diluted with CH_2Cl_2 (50 cm^3) and worked up to yield compound **14** (224 mg, 80%), v_{max}/cm^{-1} 3600–3400, 1730 and 1705; δ_H 3.65 (3 H, s, CO_2Me), 2.67 (1 H, J 14), 2.43 (1 H, s, CH), 2.4 (1 H, J 15), 2.3 (1 H, s, OH), 2.22 (1 H, dd, J 10.3 and 2.4), 1.97–1.27 (6 H, m, 3 × CH_2), 1.77 (3 H, s, Me) and 0.81 (3 H, s, Me) (Found: M$^+$, 280.1664. Calc. for $C_{16}H_{24}O_4$: M, 280.1674).

Methyl 3,6,8-Trimethyl-4-oxotricyclo[5.3.1.0³·⁸]undec-5-ene-2-carboxylate **15**.—To PTSA (0.1 g) adsorbed on silica gel (3 g) was added a solution of the alcohol **14** (140 mg, 0.5 mmol) in dry benzene (15 cm^3) and the mixture was stirred at room temperature for 12 h, then was filtered, and the benzene solution was worked up to afford pure unsaturated keto ester **15** (118 mg, 90%), v_{max}/cm^{-1} 1730 and 1680; δ_H 5.59 (1 H, d, J 1.2, vinylic), 3.54 (3 H, s, CO_2Me), 2.35 (1 H, s), 2.16–2.09 (2 H, m, bridgehead and allylic H), 1.93–1.28 (6 H, m, 3 × CH_2), 1.87 (3 H, d, J 1.3, Me), 1.25 (3 H, s, Me) and 0.82 (3 H, s, Me); δ_C 201.5 (s), 173.3 (s), 162.5 (s), 121.9 (d), 52.4 (d), 51.2 (q), 48.5 (s), 44.8 (d), 37.6 (s), 29.5 (t), 28.2 (t), 27.4 (t), 26.2 (t), 22.7 (q), 21.8 (q) and 20.1 (q) (Found: M$^+$, 262.1589. Calc. for $C_{16}H_{22}O_3$: M, 262.1569).

Methyl 3,6,8-Trimethyl-4-oxotricyclo[5.3.1.0³·⁸]undecane-2-carboxylate **16**.—The ester **15** (100 mg) was hydrogenated in the presence of 10% Pd–C catalyst (40 mg) in ethanol (10 cm^3). After 6 h the catalyst was filtered off and the solvent was evaporated off to afford the saturated ester **16** (95 mg), m.p. 60–64 °C; v_{max}/cm^{-1} 1730 and 1710; δ_H 3.59 (s, 3 H, CO_2Me), 2.09–1.25 (11 H, m), 1.19 (3 H, s, Me), 0.88 (3 H, d, J 6, Me) and 0.7 (3 H, s, Me) (Found: M$^+$, 264.1726. Calc. for $C_{16}H_{24}O_3$; M, 264.1725).

1,2,8-Trimethyl-5-oxatetracyclo[7.4.0.0²·⁶.0³·¹¹]tridecan-4-one **17**.—Sodium borohydride (35 mg) was added in small portions to a solution of the keto ester **16** (80 mg) in ice-cold ethanol (5 cm^3) and the mixture was stirred for 4 h at room temperature before being worked up to afford the lactone **17** (61 mg, 87%), which was recrystallised from methylene dichloride, m.p. 156–157 °C (lit.,³ 155–157 °C); v_{max}/cm^{-1} 1760; δ_H 4.38 (1 H, dd, J 10 and 5), 2.32–2.2 (1 H, m), 2.1 (1 H, br s, bridgehead H), 2.0 (1 H, s), 1.91 (1 H, m), 1.67–1.2 (8 H, m), 1.1 (3 H, s, Me), 0.83 (3 H, d, J 6, Me) and 0.82 (3 H, s, Me) (Found: C, 76.8; H, 9.5. Calc. for $C_{15}H_{22}O_2$: C, 76.9; H, 9.4%).

Methyl 3,6,8-Trimethyltricyclo[5.3.1.0³·⁸]undec-4-ene-2-carboxylate **18**.—Thionyl dichloride (62 mg) was added dropwise to a solution of the lactone **17** (20 mg) in methanol (4 cm^3) at room temperature and the mixture was stirred for 14 h. Methanol was removed to yield the product **18** (20 mg, 90%), v_{max}/cm^{-1} 1740; δ_H 5.27 (1 H, d, J 10), 5.12 (1 H, dd, J 10 and 2.5, CH), 3.58 (3 H, s, CO_2Me), 2.38–0.88 (10 H, m), 1.05 (3 H, s, Me), 0.85 (3 H, d, J 7.4, Me) and 0.6 (3 H, s, Me).

Methyl 3,6,8-*Trimethyltricyclo*[5.3.1.0^{3,8}]*undecane-2-carboxylate* **19**.—The unsaturated ester **18** (16 mg) and Pd–C (10%; 20 mg) were stirred in ethanol (2 cm^3) under hydrogen for 6 h. The catalyst was filtered off and the filtrate was evaporated to obtain the pure product **19** (15 mg, 95%), v_{max}/cm^{-1} 1730; δ_H 3.6 (3 H, s, CO$_2$Me), 2.16 (1 H, s), 1.96–0.88 (13 H, m), 0.96 (3 H, s, Me), 0.72 (3 H, s, Me) and 0.68 (3 H, d, *J* 4, Me) (Found: M$^+$, 250.1932. Calc. for C$_{16}$H$_{26}$O$_2$: *M*, 250.1933).

2-*Hydroxymethyl*-3,6,8-*trimethyltricyclo*[5.3.1.0^{3,8}]*undecane* **20**.—A solution of the saturated ester **19** (12 mg) in dry diethyl ether (1 cm^3) was added to a suspension of LiAlH$_4$ (20 mg) in dry diethyl ether (2 cm^3) at 0 °C and the mixture was stirred for a further 5 h, quenched with saturated aq. NH$_4$Cl, and worked up to give the alcohol **20** (9.8 mg, 92%), v_{max}/cm^{-1} 3700–3300; δ_H 4.05–3.45 (2 H, m), 2.28–1.0 (15 H, m), 0.87 (3 H, s, Me), 0.79 (3 H, d, *J* 6, Me) and 0.77 (3 H, s, Me) (Found: C, 82.0; H, 11.8. Calc. for C$_{15}$H$_{26}$O: C, 81.8; H, 11.7%).

Seychellene **1**.—To a stirred solution of the alcohol **20** (8 mg) in dry THF (2 cm^3) at 0 °C were added triethylamine (15 mg) and then methanesulfonyl chloride (8 mg). After 2 h, the reaction mixture was filtered, and washed with THF. After concentration, and redissolution of the residue in toluene (3 cm^3), DBU (27 mg) was added and the reaction mixture was refluxed for 4 h, diluted with benzene (30 cm^3), and worked up to give the crude product, which was purified by passage through a short column of silica gel. Elution with hexane afforded seychellene **1** (5.1 mg, 70%), v_{max}/cm^{-1} 1644 and 800; δ_H 4.58 (1 H, d, *J* 1.4, vinylic), 4.58 (1 H, d, *J* 1.4, vinylic), 2.3–2.1 (1 H, m, CHC=), 0.96 (3 H, s, Me), 0.88 (3 H, s, Me) and 0.75 (3 H, d, *J* 6.7, Me) (Found: M$^+$, 204.1877. Calc. for C$_{15}$H$_{24}$: *M*, 204.1878).

Acknowledgements

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