Synthetic Studies towards the Pinguisanes; Synthesis of 4-*epi*-Pinguisone

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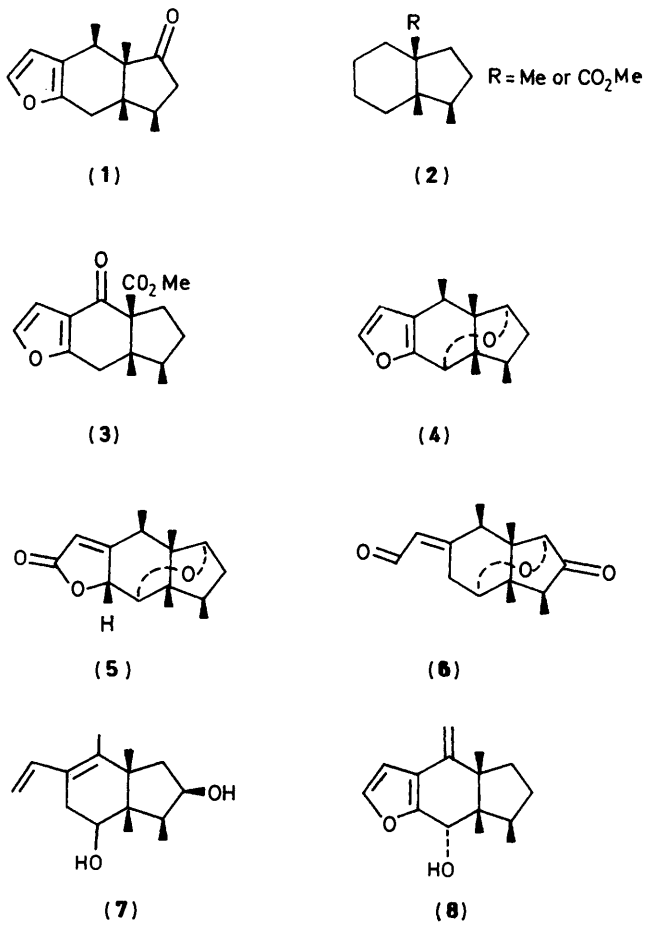
Two procedures have been developed for the synthesis of the appropriate indene skeleton required for construction of pinguisone and 4-*epi*-pinguisone. Whereas 1-methoxy-3-(trimethylsiloxy)buta-1,3-diene (Danishefsky's diene) was completely unreactive towards 2,3,4-trimethyl-2-cyclopent-2-en-1-one, Diels–Alder cycloaddition was found to occur at very high pressure (13—15 kBar) with the more reactive dienophile methyl 2,3-dimethyl-5-oxocyclopent-1-ene-1-carboxylate giving, after hydrolysis, (3*R**,3a*S**,7a*R**)-methyl 2,3,3a,7a-tetrahydro-3,3a-dimethyl-1,5(4*H*)-dioxoindene-7a-carboxylate in good yield. The structure of this compound was confirmed by *X*-ray diffraction. Reaction of the lithium enolate of the diene with the more reactive dienophile at low temperatures gave one Michael addition only; however, the resulting oxo ester was converted into the desired indene intermediate in a good overall yield. Model studies provided a route which, when applied to the indene intermediate, enabled an efficient conversion to (3*R**,3a*S**,7a*S**)-2,3,3a,7a-tetrahydro-3,3a,7a-trimethylindene-1,5(4*H*)-dione. Conjugate addition with lithium dimethylcuprate gave the undesired epimer exclusively which on further elaboration gave 4-*epi*-pinguisone and 4-*epi*-pinguisanol.

In 1969 Benesova and co-workers isolated pinguisone,[1,2] a crystalline furanosesquiterpene from the essential oil of the liverwort, *Aneura pinguis* (L). It was assigned the tricyclic structure (**1**) and the structure was confirmed and its absolute configuration established by *X*-ray analysis of the *p*-bromobenzylidene.[3] Pinguisone was the first of a new class of sesquiterpenes which now number twenty-two,[4–27] all of which have a six-five bicyclic structure (**2**) with the three methyl groups in a *cis* configuration. However, they show a remarkable degree of diversity containing between them such functional groups as furan, butenolides, ketones, alcohols, esters, ethers, dienes, and an aldehyde, *e.g.*, compounds (**3**)—(**8**). Of the isolated pinguisanes only pinguisone (**1**) itself has any reported activity showing antifeedant activity at concentrations of 0.125% for ten day old larvae of *Spodoptera littoralis*, the cotton leafworm.[28]

Although pinguisone was our initial target, we recognised at the outset that our synthetic strategy might result in a synthesis of 4-*epi*-pinguisone. Nevertheless our general approach would, we felt, generate important intermediates for synthesis of pinguisane derivatives.

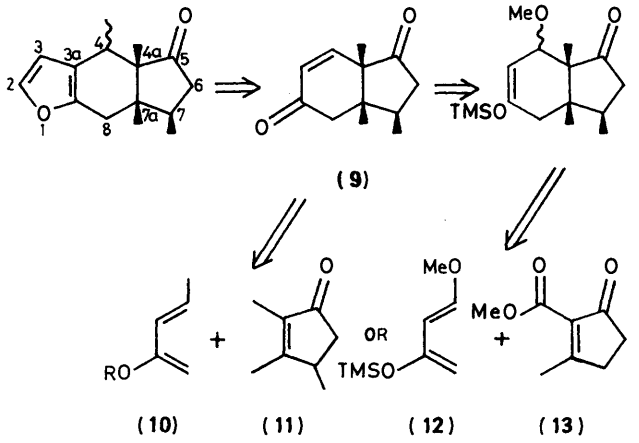
To date, two total syntheses of pinguisone (**1**) and deoxypinguisone have been published. Jommi *et al*[29] built up the correct stereochemistry by the stepwise introduction of three of the four methyl groups using cuprate additions to α,β-unsaturated ketones. More recently Uyehara *et al*[30] have generated the required six-five structure *via* a 1,3-acyl shift on direct photochemical excitation[31–35] of a bicyclo[3.2.2]non-6-en-2-one. A synthesis of 7-*epi*-pinguisone from (*S*)-(+)-2,3,7,7a-tetrahydro-7a-methylindene-1,5(6*H*)-dione has also been described.[36]

Any proposed synthesis of the pinguisanes must have as its first objective the construction of the indene carbon skeleton with the correct stereochemical relationship between the adjacent methyl groups. Retrosynthetic analysis yielded the bicyclic structure (**9**) as a key intermediate. In a subsequent step, introduction of the 4-methyl substituent followed by introduction of the furan derivative would lead to either pinguisone or 4-*epi*-pinguisone. In the event dimethylcuprate addition to (**9**) proceeded exclusively from the α-face yielding an intermediate which was converted to 4-*epi*-pinguisone. In this paper we describe two approaches to the synthesis of indene (**9**) and its subsequent conversion to 4-*epi*-pinguisone.

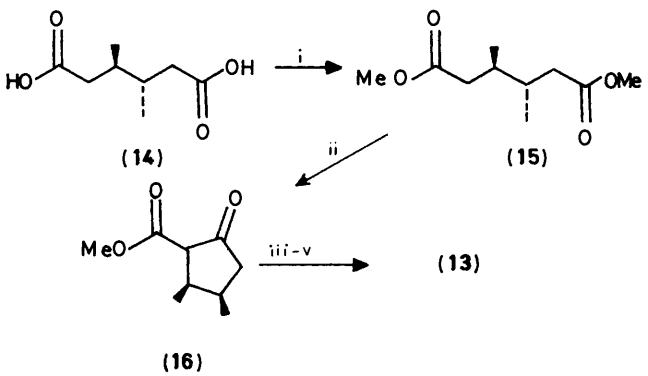


1. *The Diels–Alder Approach.*—In theory the required bicyclic intermediate (**9**) could be constructed *via* the cycloaddition

reaction between the diene (**10**) and 2,3,4-trimethylcyclopent-2-enone (**11**). However, a brief survey of the literature showed that cyclopentanones are unreactive dienophiles[37] and, in particular, the introduction of a β-alkyl substituent markedly decreases their reactivity.[38] In addition it might be expected that the favoured *endo* addition would give rise to the undesired epimer at C-4. For these reasons an alternative cycloaddition between 'Danishefsky's diene'[39] (**12**) and the doubly-activated dienophile (**13**), was utilised.



The required dienophile (**13**) was prepared from the diacid (**14**) which was, in turn, obtained from tetrahydrophthalic anhydride by literature procedures.[40,41] Esterification using methanol and chlorotrimethylsilane[42] yielded the diester (**15**) in 90% yield. Dieckmann cyclisation to the oxoester (**16**) followed by selenylation/elimination[43] yielded the required oxoester (**13**) (Scheme 1). Initial attempts to achieve cycloaddition under



Scheme 1. *Reagents and conditions:* i, MeOH, TMSCl; ii, NaH, DME, 65 °C; iii, NaH; iv, PhSeCl; v, H_2O_2

thermal conditions were not encouraging since heating the diene (**12**) and the dienophile (**13**) in a sealed tube at a variety of temperatures in a variety of solvents yielded either starting materials or decomposition. However, heating the dienophile with six equivalents of the dienophile at 155 °C for 24 h in the absence of solvent gave, on acid hydrolysis, an 18% yield of a 3:1 mixture of the adducts (**17**) and (**18**). In an attempt to enhance the yield of this reaction the use of Lewis acid catalysis was investigated, but no improvement was observed. However, the yield was greatly improved by the use of high pressure conditions.

The oxoester (**13**) and a threefold excess of the diene (**12**) in methylene dichloride was pressurised at 13 kbar at 35 °C for seven days. This gave an unstable yellow oil

Table 1. Fractional atomic co-ordinates for compound (**17**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
C(1)	0.817 0(2)	0.917 9(2)	0.377 8(2)
C(2)	0.805 7(2)	1.238 2(2)	0.390 0(1)
C(3)	0.824 4(2)	1. 068 7(2)	0.443 1(1)
C(4)	0.588 5(2)	1.299 4(3)	0.368 7(1)
O(5)	0.543 4(1)	1.180 7(2)	0.423 7(1)
C(6)	0.671 2(2)	1 062 9(3)	0.274 9(2)
O(7)	0.551 8(1)	1.440 9(2)	0.361 6(1)
C(8)	0.695 6(2)	1.2353(2)	0.320 0(1)
O(9)	0.879 6(2)	0.795 0(2)	0.388 5(1)
C(10)	0.726 4(2)	0.922 3(3)	0.299 0(2)
C(11)	0.797 6(2)	1.376 4(3)	0.468 2(1)
C(12)	0.852 9(2)	0.399 0(3)	0.244 7(2)
O(13)	0.660 8(2)	1.391 1(3)	0.167 5(1)
C(14)	0.904 2(2)	1.274 4(2)	0.317 7(1)
C(15)	0.727 7(2)	1.352 5(3)	0.233 9(1)
C(16)	0.444 9(2)	1.224 0(3)	0.480 6(2)
C(17)	1.018 3(2)	1.332 4(4)	0.365 7(2)
H(3A)	0.757(2)	1.061(2)	0.491(1)
H(3B)	0.899(2)	1.072(2)	0.476(1)
H(6)	0.610(2)	1.076(3)	0.225(2)
H(10)	0.707(2)	0.815(2)	0.262(2)
H(11A)	0.863(2)	1.370(3)	0.514(1)
H(11B)	0.729(2)	1.354(3)	0.512(1)
H(11C)	0.782(2)	1.479(3)	0.447(1)
H(12A)	0.861(2)	1.512(3)	0.266(1)
H(12B)	0.888(2)	1.381(3)	0.187(1)
H(14)	0.918(2)	1.178(2)	0.285(1)
H(16A)	0.412(2)	1.130(4)	0.519(2)
H(16B)	0.397(2)	1.285(3)	0.450(2)
H(16C)	0.461(2)	1.308(3)	0.552(2)
H(17A)	1.072(2)	1.357(3)	0.318(2)
H(17B)	1.042(2)	1.260(3)	0.417(2)
H(17C)	1.001(2)	1.448(3)	0.406(2)

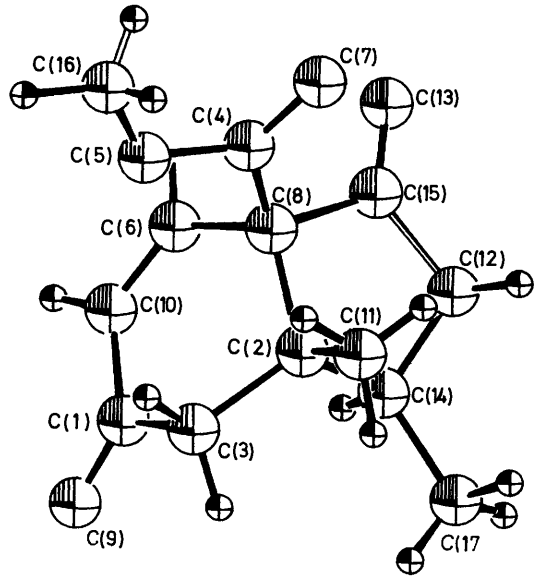
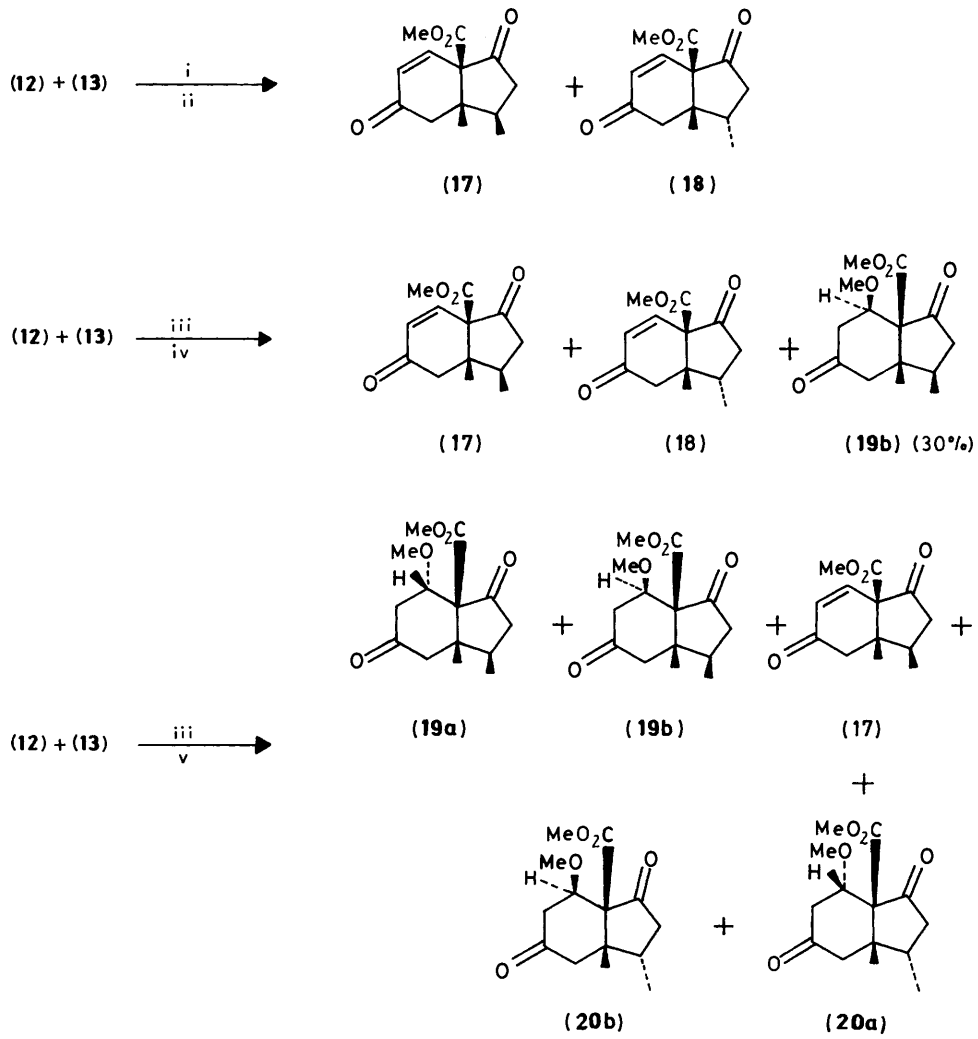


Figure. ORTEP diagram of the indene intermediate (**17**)

which, on treatment with tetrabutylammonium fluoride, gave four products identified as the isomeric β-methoxy ketones (**19a**), (**19b**), (**20a**), and (**20b**) and the enone (**17**) in a combined yield of 91%. Repetition of the cycloaddition followed by acid hydrolysis of the intermediate silyl enol ether gave a 4:1 ratio of the enones (**17**) and (**18**) in a combined yield of 55%

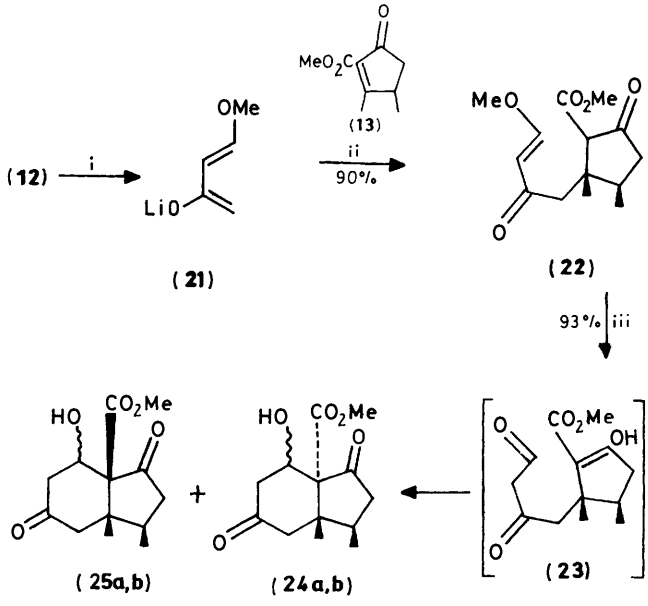


Scheme 2. *Reagents and conditions:* i, Heat 155 °C, 24 h; ii, H_3O^+; iii, 13 kBar, 35 °C; iv, CSA; v, Bu^4NF

together with a 30% yield of (**19b**) (Scheme 2). Increasing the pressure to 15 kbar resulted in a loss in (3:1) selectivity between the enones (**17**) and (**18**). The structure of enone (**17**) was confirmed by *X*-ray analysis and the molecular structure is shown in the ORTEP diagram (Figure). The fractional atomic co-ordinates and the bond lengths and bond angles for compound (**17**) are summarised in Tables 1 and 2.

2. *The Double-Michael Approach.*—One approach to increasing the reactivity of the diene is to form the lithium dienolate so that the subsequent cycloaddition reaction can then be depicted as involving two sequential Michael additions.[44,45] Accordingly the diene (**12**) was treated with methyl-lithium at −40 °C in tetrahydrofuran, but only very slow formation of the enolate (**21**) occurred and the enolate produced was not stable under these conditions. Changing the solvent to dimethoxyethane[46] resulted in a dramatic improvement in both the rate of enolate formation and stability. Treatment of the dienolate (**21**) with the oxoester (**13**) gave a single product in 90% yield. However, inspection of the spectral data indicated that only the first Michael addition had occurred, yielding the product (**22**) (Scheme 3). Attempts to achieve the second Michael addition using a variety of bases were unsuccessful.

Cyclisation of the enone (**22**) was then attempted under acidic conditions, in the hope that acid hydrolysis would yield the



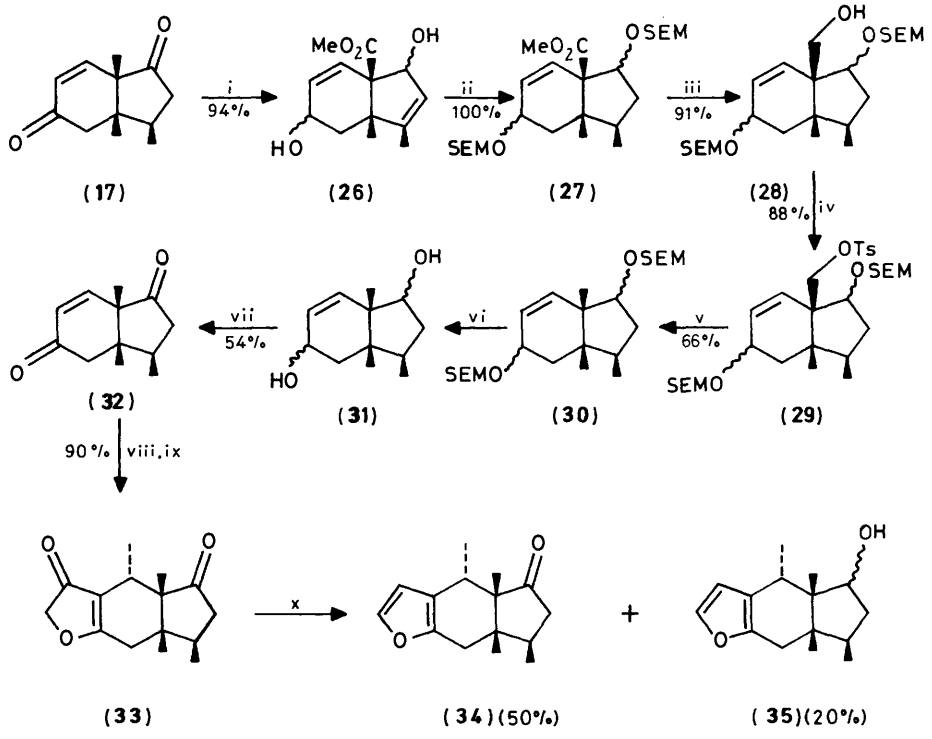
Scheme 3. *Reagents and conditions:* i, MeLi, DME, −50 °C; ii, −90 °C, THF; iii, H_3O^+

Table 2. Bond lengths (Å) and bond angles (°) for compound (**17**) with e.s.d.s in parentheses

Bond lengths			
C(1)–C(3)	1.487(3)	C(4)–C(8)	1.514(3)
C(1)–O(9)	1.217(3)	O(5)–C(16)	1.442(3)
C(1)–C(10)	1.472(3)	C(6)–C(8)	1.517(3)
C(2)–C(3)	1.534(3)	C(6)–C(10)	1.318(3)
C(2)–C(8)	1.563(3)	C(8)–C(15)	1.548(3)
C(2)–C(11)	1.529(3)	C(12)–C(14)	1.506(3)
C(2)–C(14)	1.558(3)	C(12)–C(15)	1.496(3)
C(4)–O(5)	1.319(3)	O(13)–C(15)	1.207(3)
C(4)–O(7)	1.199(3)	C(14)–C(17)	1.523(3)
Bond angles			
C(3)–C(1)–O(9)	123.2(2)	C(2)–C(8)–C(4)	112.9(2)
C(3)–C(1)–C(10)	116.1(2)	C(2)–C(8)–C(6)	113.3(2)
O(9)–C(1)–C(10)	120.7(2)	C(2)–C(8)–C(15)	103.9(1)
C(3)–C(2)–C(8)	111.8(1)	C(4)–C(8)–C(6)	109.5(2)
C(3)–C(2)–C(11)	107.9(1)	C(4)–C(8)–C(15)	110.7(2)
C(3)–C(2)–C(14)	111.3(1)	C(6)–C(8)–C(15)	106.2(2)
C(8)–C(2)–C(11)	111.4(1)	C(1)–C(10)–C(6)	121.8(2)
C(8)–C(2)–C(14)	102.5(1)	C(14)–C(12)–C(15)	105.1(2)
C(11)–C(2)–C(14)	111.9(2)	C(2)–C(14)–C(12)	104.9(2)
C(1)–C(3)–C(2)	114.6(2)	C(2)–C(14)–C(17)	115.3(2)
O(5)–C(4)–O(7)	124.3(2)	C(12)–C(14)–C(17)	113.6(2)
O(5)–C(4)–C(8)	110.9(2)	C(8)–C(15)–C(12)	109.3(2)
O(7)–C(4)–C(8)	124.7(2)	C(8)–C(15)–O(13)	123.5(2)
C(4)–O(5)–C(16)	118.1(2)	C(12)–C(15)–O(13)	127.1(2)
C(8)–C(6)–C(10)	125.2(2)		

aldehyde (**23**) which would then undergo intramolecular aldol condensation. After much experimentation it was found that the most effective method was treatment of the enone (**22**) with 0.02M HCl (aq.) in tetrahydrofuran (1:1 v/v) for 3 h. Under these conditions, the β-hydroxy ketones (**24a** and **b**) and (**25a** and **b**) could be isolated in 93% yield (Scheme 3). Elimination of the β-hydroxy group required careful examination but conditions were eventually found which gave the enone (**17**) in an overall yield of 56% from dienophile (**13**). The minor product, enone (**18**), was usually observed in small quantities, the ratio of (**17**):(**18**) being typically 15:1. No *trans*-fused enone was ever observed even though both *cis*- and *trans*-fused ring junctions are produced in the intramolecular aldol reaction. Only the former of these undergoes elimination due to strain factors in the latter. The most favoured conditions for the elimination proved to be reaction with phosphorus oxychloride in the presence of an excess of methanesulphonyl chloride and *N*,*N*-isopropylethylamine in methylene dichloride for 3 h at −10 °C. The reaction probably involves methanesulphonylation prior to elimination. With the synthesis of the key indene skeleton in hand we turned our attention towards a synthesis of pinguisone (**1**).

Elaboration towards Pinguisone.—Two key transformations, reduction of the sterically hindered ester to a methyl and the introduction of the furan ring remained to complete the total synthesis of pinguisone (**1**). Initial studies on the conjugate addition of dimethyl cuprate to enone (**17**) not surprisingly gave a large number of unidentified products, clearly the propensity of a retro-Michael reaction means that the ester would have to be reduced prior to cuprate addition. Protection of the two ketone entities was necessary prior to reduction of the ester. Attempts to form the bisacetal were unsuccessful, so the enone (**17**) was reduced with sodium borohydride and ceric (III) chloride in methanol to give diol (**26**) as a mixture of four diastereoisomers (Scheme 4). Protection of the diol as the bis(SEM) ether (**27**), ester reduction to yield the primary alcohol (**28**) and toluene-*p*-sulphonylation (**29**) then proceeded uneventfully with a typical overall yield of the toluene-*p*-sulphonate (**29**) from enone (**17**) of 75%. Examination of molecular models suggested that the reduction may well be



Scheme 4. *Reagents and conditions:* i, $NaBH_4$, $CeCl_3$, MeOH, RT; ii, SEMCl, Pr^iNEt_2, CH_2Cl_2; iii, $LiAlH_4$, THF, RT; iv, *p*-TsCl, py, DMAP (1 equiv.), RT; v, NaI, Zn, HMPA, 110 °C; vi, TBAF, HMPA, 85 °C; vii, PCC, CH_2Cl_2; viii, Me_2CuLi; ix, $ClCH_2COCl$; x, 9-BBN, 0 °C

difficult due to the severe steric hindrance surrounding the toluene-*p*-sulphonate functionality. Our worst fears were realised when reduction of the very hindered toluene-*p*-sulphonate (**29**) was attempted in that the use of lithium aluminium hydride gave mainly the alcohol (**28**) with a small amount of the required alkene (**30**) (ratio 5:1) in a combined yield of 60%. The more nucleophilic reducing agent lithium triethylborohydride improved the combined yield to 98% but gave a ratio of 8:1. A variety of other methods of reduction such as tributyltin hydride reduction of the xanthate, photolysis of the acetate and toluene-*p*-sulphonate in HMPA, and a variety of other hydride reductions were tried without success. Conversion to the analogous methanesulphonate or alcohol and subsequent reactions also met with failure. In due course the procedure of Fujimoto and Tatsuno[47] involving zinc reduction of the *in situ* generated iodide proved successful, yielding the required alkene (**30**) in 66% yield. Remarkably, in view of this success over all other methods attempted, this is one of the least used methods in organic synthesis for such reductions. Attempted deprotection using dimethylboron bromide failed to yield the required diol. However, treatment with tetrabutylammonium fluoride in hexamethylphosphoramide gave the diol (**31**) in 46% yield. PCC Oxidation gave the diketone (**32**).

We now turned our attention to the introduction of the furan ring. Treatment of the enone (**32**) with lithium dimethylcuprate and acylation of the intermediate enolate at −55 °C with chloroacetyl chloride yielded a *single* product (**33**) in 90% yield; no trace was observed of any other diastereoisomer. At this point the stereochemistry at C-4 could not be unambiguously assigned. However, reduction with 9-borabicyclononane (9-BBN) at 0 °C was not surprisingly, regioselective and a mixture of two products was obtained, which were identified as 4-*epi*-pinguisone (**34**) and 4-*epi*-pinguisanol confirming that the β-furanone had the structure (**33**). Obviously the steric crowding on the β-face was sufficiently great to overcome the convex shape of the molecule and so only α-addition of the cuprate was observed. The structure of 4-*epi*-pinguisone can be confidently assigned on the basis of a comparison of the ^{1}H n.m.r. spectra of 4-*epi*-pinguisone (**34**) and pinguisone (**1**)[2] since the *X*-ray analysis of enone (**17**) established the relative stereochemistry of the other three methyl groups. Several significant differences were noted in the ^{1}H n.m.r. spectra of compounds (**34**) and (**1**). In particular the signal representing the 4-Me appeared at δ 1.09 and 1.16 for pinguisone and (**34**), respectively. In addition the signal for 4-H at δ 2.75 in pinguisone which is coupled to both 8-H was replaced by a signal at δ 2.57 with coupling to only one 8-H in the spectrum for compound (**34**).

Experimental

I.r. spectra were recorded on a Pye-Unicam SP3-100 spectrophotometer using polystyrene as standard. ^{1}H, ^{13}C, and ^{19}F N.m.r. spectra were recorded either on a Hitachi-Perkin-Elmer R-24B (60 MHz) spectrometer, a Varian Associates XL-100-12 (100 MHz) spectrometer or a Bruker AM-360 (360 MHz) spectrometer. Tetramethylsilane was used as standard, and deuteriochloroform used as a solvent unless otherwise stated. Mass spectra were recorded using a Kratos MS-30 spectrometer equipped with a Nova-3 computer and a DS 50S data system, using electron impact (e.i.) or chemical ionization (c.i.). M.p.s were measured on a Reichert Koffler hot stage melting point apparatus and are uncorrected. Gas liquid chromatography (g.l.c.) was performed on a Pye series 104 chromatograph equipped with a flame ionization detector. Elemental analyses were carried out by the micro-analytical laboratory, University College, London. All solvents were purified before use, light petroleum refers to the fraction boiling between 40—60 °C, and ether refers to diethyl ether. Flash chromatography was performed using Macherey-Nagel Kieselgel 60 (230—400 mesh). Methyl-lithium was used as a solution in diethyl ether as supplied by Aldrich Chemical Company.

meso-3,4-*Dimethylhexane*-1,6-*dioic Acid* (**14**).—A solution of potassium permanganate (53.8 g) in water (320 ml) was vigorously stirred with benzene (120 ml) and tetrabutylammonium hydrogen sulphate (0.6 g). A solution of *cis*-4,5-dimethylcyclohexene[41] (10.3 g, 94 mmol) in benzene (120 ml) was added dropwise over 20 min and the reaction stirred for 24 h. The solution was cooled to 0 °C and sodium sulphate (66 g) was added followed by concentrated hydrochloric acid until the brown precipitate turned white. The aqueous layer was extracted with ether (6 × 200 ml). After being dried the solvent was evaporated to give the diacid (**14**) (11.42 g, 68%) as a white solid, m.p. 130—133 °C (from water) (lit.,[41] 133—134 °C).

Dimethyl meso-3,4-*Dimethylhexane*-1,6-*dioate* (**15**).—Dry chlorotrimethylsilane (42.5 ml, 36.4 g, 0.33 mmol) was added to a solution of the diacid (**14**) (10 g, 58 mmol) in dry methanol (500 ml) under nitrogen at room temperature during 5 min. After 24 h, the solvent was evaporated and the oil dissolved in ether (250 ml). This was washed with aqueous sodium hydrogen carbonate (3 × 100 ml), dried, and the solvent evaporated to give a pale brown liquid (11.8 g). Distillation yielded the title compound (10.5 g, 91%) as a colourless oil, b.p. 60—65 °C/0.2 mmHg (Found: C, 59.2; H, 9.0. $C_{10}H_{18}O_4$ requires C, 59.4; H, 9.0%); $\nu_{max.}$ 2 965, 1 740, 1 440, 1 200, and 1 175 cm^{-1}; δ_H (360 MHz) 0.88 (6 H, d, *J* 7 Hz, 3- and 4-Me), 1.97—2.15 (4 H, m, 2-, 3-, 4-, and 5-H), 2.35 (2 H, dd, *J* 3.6 and 14.6 Hz, 2- and 5-H), and 3.68 (6 H, s, CO_2Me); δ_C (90.5 MHz) 14.8 (3-Me), 34.0 (C-3), 39.1 (C-2), 51.1 (OMe), and 173.1 (C-1): *m/z* (c.i., NH_3) 203 (MH^+, 25%), 171 (100), 139 (45), 129 (69), 97 (31), 87 (41), 69 (76), and 59 (46) (Found: MH^+, 203.1283. $C_{10}H_{19}O_4$ requires *M*H, 203.1274).

Methyl cis-2,3-*Dimethyl*-5-*oxocyclopentane*-1-*carboxylate* (**16**).—The diester (**15**) (4 g, 19.8 mmol) in dimethoxyethane (DME) (40 ml) was added to a solution of sodium hydride (1.5 g, 62.5 mmol) in dry DME (160 ml) under nitrogen. The solution was heated under reflux for 48 h, cooled to 0 °C, and aqueous sodium dihydrogen orthophosphate (150 ml) carefully added. Following ether extraction (3 × 150 ml) the combined extracts were washed with brine (50 ml), dried, and the solvent evaporated to give a brown oil which was distilled to yield the title compound (**16**) as a colourless liquid (2.52 g, 75%), b.p. 70—72 °C/0.2 mmHg (Found: C, 63.6; H, 8.3. $C_9H_{14}O_3$ requires C, 63.5; H, 8.3%); $\nu_{max.}$ 1 760, 1 731, and 1 280 cm^{-1}; δ_H (100 MHz) 0.96 (3 H, d, *J* 10 Hz, 3-Me), 1.12 (3 H, d, *J* 10 Hz, 2-Me), 2.04—3.00 (5 H, 1-, 2-, and 3-H, and 4-H_2), and 3.77 (3 H, s, CO_2Me); δ_C (25.1 MHz), 14.9 (2- and 3-Me), 32.2 (C-3), 38.8 (C-2), 47.0 (C-4), 52.3 (OMe), 59.7 (C-1), 169.8 (CO_2), and 211.7 (C-5); *m/z* (c.i.) 170 (M^+, 1%), 142 (12), 139 (9), 101 (64), 86 (36), 85 (19), 69 (100), 68 (13), and 55 (16) (Found: M^+, 170.0967. $C_9H_{14}O_3$ requires *M*, 170.0943).

Methyl 2,3-*Dimethyl*-5-*oxocyclopent*-1-*ene*-1-*carboxylate* (**13**).—Benzeneselenyl chloride (2.5 g, 13 mmol) was added to a solution of the oxoester (**16**) (2 g, 11.8 mmol) and sodium hydride (360 ml, 15 mmol) in dry THF (60 ml) at 0 °C in one portion with vigorous stirring. After 10 min the reaction mixture was added to a mixture of ether–light petroleum–aqueous sodium hydrogen carbonate (2:2:1, 100 ml). The aqueous layer was separated and back extracted with ether (50 ml). The combined extracts were washed with brine (20 ml), dried, and the solvent evaporated to give methyl *cis*-2,3-dimethyl-5-oxo-1-phenylselenocyclopentane-1-carboxylate as an orange oil; δ_H (60

MHz) 0.92 (3 H, d, *J* 7 Hz, 3-Me), 1.04 (3 H, d, *J* 7 Hz, 2-Me), 1.6—2.9 (4 H, m, 2- and 3-H, and 4-H_2), 3.65 (3 H, s, CO_2Me), and 7.1—7.8 (5 H, m, Ph). This was dissolved in methylene dichloride (80 ml) under nitrogen and hydrogen peroxide (15% w/v; 7 ml, 31 mmol) was added until a very vigorous exothermic reaction commenced at which point the reaction was quickly cooled to 0 °C. After 30 min the aqueous layer was separated, the organic layer was diluted with methylene dichloride (50 ml) and washed with aqueous sodium hydrogen carbonate (2 × 20 ml), brine (20 ml), dried, and the solvent evaporated to give a pale yellow oil. Chromatography on flash silica gel with ether–light petroleum (3:1) as eluant yielded an oil which was distilled giving the title compound (**13**) as a colourless oil (1.44 g, 73%), b.p. (Kugelrohr) 60 °C/0.25 mmHg; $\nu_{max.}$ 1 745, 1 715, 1 255, and 1 230 cm^{-1}; δ_H (100 MHz) 1.25 (3 H, d, *J* 10 Hz, 3-Me) and 3.75 (3 H, s, CO_2Me); δ_C (25.1 MHz) 17.0 (C-Me), 18.6 (2-Me), 38.3 (C-3), 43.7 (C-4), 51.7 (OMe), 131.9 (C-1), 163.9 (C-2), 188.7 (CO_2), and 202.5 (C-5); *m/z* (e.i.) 168 (M^+, 30%), 138 (30), 137 (83), 136 (46), 110 (29), 80 (21), 69 (100), and 67 (32) (Found: M^+, 168.0794. $C_9H_{12}O_3$ requires *M*, 168.0786).

Methyl 2,3,3a,6,7,7a-*Hexahydro*-7-*methoxy*-3,3a-*dimethyl*-1,5 (4H)-*dioxoindene*-7a-*carboxylate* (**19a,b**) *and* (**20a,b**).—A solution of the oxo ester (**13**) (136 mg, 0.81 mmol) and the diene (**12**) (300 mg, 1.74 mmol; 2.2 equiv.) in dry methylene dichloride (3 ml) was kept at a pressure of 13 kBar at 35 °C for 7 days. The solvent was removed to give (3a*S**,7a*S**)-methyl-2,3,3a,4,7,7a-hexahydro-7-methoxy-3,3a-dimethyl-1-oxo-5-trimethylsiloxy-indene-7a-carboxylate as a yellow oil (270 mg, 98%); δ_H (60 MHz) 0.25 (9 H, s, $SiMe_3$), 0.85 (3 H, s, 3a-Me), 1.00 (3 H, d, *J* 7 Hz, 3-Me), 1.35—2.95 (5 H, m, 2-H_2, 3-H, and 4-H_2), 3.25 and 3.35 (3 H, 2 × s, 7-OMe), 3.70 and 3.75 (3 H, 2 × s, CO_2Me), 3.8—4.7 (1 H, br, 7-H), and 5.1 (1 H, br, 6-H).

The enol ether was dissolved in methylene dichloride (10 ml) and tetrabutylammonium fluoride [3 mmol; 1M in tetrahydrofuran (THF)] was added. After 10 min aqueous sodium dihydrogen orthophosphate (10 ml) was added and the solution extracted with ether (2 × 100 ml). The combined extracts were washed with aqueous sodium hydrogen carbonate (10 ml), brine (10 ml), dried, and the solvent evaporated to give a pale brown oil. Chromatography (ether–light petroleum) (3:2–neat ether) as eluant gave four fractions (all white, crystalline solids).

(i) (3S*,3aS*,7S*,7aS*)- *and* (3S*,3aS*,7R*,7aS*)-*Methyl* 2,3,3a,6,7,7a-*Hexahydro*-7-*methoxy*-3,3a-*dimethyl*-1,5(4H)-*dioxoindene*-7a-*carboxylate* (**20a**) *and* (**20b**) (28 mg, 13%), m.p. 78—82 °C (ether–petroleum) (Found: C, 62.6; H, 7.4. $C_{14}H_{20}O_5$ requires C, 62.7; H, 7.5%); $\nu_{max.}$ 1 750, 1 725, and 1 260 cm^{-1}; δ_H (60 MHz) 1.00 (3 H, d, *J* 7 Hz, 3-Me), 1.05 (3 H, s, 3a-Me), 1.9—3.0 (7 H, m, 2-H_2, 3-H, and 6-H_2), 3.21 (1.2 H, s, 7-OMe), 3.29 (1.8 H, s, 7-OMe), 3.73 (1.2 H, s, CO_2Me), 3.75 (1.8 H, s, CO_2Me), 4.17 (0.4 H, t, *J* 4 Hz, 7-H), and 4.35 (0.6 H, t, *J* 4 Hz, 7-H); *m/z* (e.i.) 268 (M^+, 4%), 168 (47), 167 (84), 137 (75), 136 (53), 135 (70), 79 (97), 69 (56), and 43 (100) (Found: M^+, 268.1334. $C_{14}H_{20}O_5$ requires *M*, 268.1310).

(ii) (3R*,3aS*,7aR*)-*Methyl* 2,3,3a,7a-*Tetrahydro*-3,3a-*dimethyl*-1,5(4H)-*dioxoindene*-7a-*carboxylate* (**17**) (6 mg, 3%), m.p. 82 °C (chloroform–pentane) (Found: C, 66.1; H, 6.9. $C_{13}H_{16}O_4$ requires C, 66.1; H, 6.8%); $\nu_{max.}$ 1 765, 1 755, 1 735, 1 690, 1 620, and 1 250 cm^{-1}; $\lambda_{max.}$(EtOH) 221 (ε 4 900 dm^3 mol^{-1} cm^{-1}) and 240 nm (3 500); δ_H (360 MHz) 0.96 (3 H, s, 3a-Me), 0.98 (3 H, d, *J* 6.4 Hz, 3-Me), 2.11 (1 H, ddq, *J* 6.4, 6.6, and 12.6 Hz, 3-H), 2.22 (1 H, dd, *J* 12.6 and 18.0 Hz, 2β-H), 2.41 (1 H, dd, *J* 6.6 and 18 Hz, 2α-H), 2.46 (1 H, d, *J* 16.8 Hz, 4β-H), 2.51 (1 H, br d, *J* 16.8 Hz, 4α-H), 3.70 (3 H, s, CO_2Me), 6.12 (1 H, dd, *J* 0.5 and 10 Hz, 6-H), and 6.40 (1 H, d, *J* 10 Hz, 7-H); δ_C (90.5 Hz), 12.9 (3-Me), 19.0 (3-Me), 35.0 (C-3), 43.7 (C-2 or C-4), 44.0 (C-2 or C-4), 44.6 (C-3a), 52.6 (OMe), 67.9 (C-7a), 130.7 (C-6), 142.2 (C-7), 168.2 (CO_2), 196.6 (C-5), and 208.1 (C-1); *m/z* (e.i.) 236 (M^+, 15%), 167 (6), 136 (6), 135 (100), 134 (8), 107 (6), 79 (15), and 69 (8) (Found: M^+, 236.1020. $C_{13}H_{16}O_4$ requires *M*, 236.1049).

(iii) (3R*,3aS*,7S*,7aS*)-*Methyl* 2,3,3a,6,7,7a-*Hexahydro*-7-*methoxy*-3,3a-*dimethyl*-1,5(4H)-*dioxoindene*-7a-*carboxylate* (**19a**) (87 mg, 40%), m.p. 83—85 °C (ether–petroleum) (Found: C, 62.3; H, 7.5. $C_{14}H_{20}O_5$ requires C, 62.7; H, 7.5%); $\nu_{max.}$ 1 750, 1 720, 1 120, and 1 090 cm^{-1}; δ_H (100 MHz) 0.96 (3 H, s, 3a-Me), 1.00 (3 H, d, *J* 7 Hz, 3-Me), 1.89—2.82 (6 H, m, 2-H_2, 3-H, 4-H_2, and 6β-H), 3.16 (1 H, m, 6α-H), 3.20 (3 H, s, 7-OMe), 3.78 (3 H, s, CO_2Me), and 4.12 (1 H, t, *J* 4 Hz, 7-H); δ_C (25.1 MHz) 13.6 (3-Me), 21.3 (3a-Me), 36.5 (C-3), 41.6 (C-2 or C-4), 45.6 (C-2 or C-4), 48.1 (C-6), 49.0 (C-3a), 52.1 (7-OMe), 57.7 (CO_2Me), 65.9 (C-7a), 82.6 (C-7), 170.7 (CO_2), 208.3 (C-5), and 211.4 (C-1); *m/z* (c.i., NH_3) 286 (MNH_4^+, 15%), 269 (MH^+, 100), 169 (87), 168 (37), 167 (25), 137 (25), 100 (71), and 85 (46).

(iv) (3R*,3aS*,7R*,7aS*)-*Methyl* 2,3,3a,6,7,7a-*Hexahydro*-7-*methoxy*-3,3a-*dimethyl*-1,5(4H)-*dioxoindene*-7a-*carboxylate* (**19b**) (74 mg, 35%), m.p. 118 °C (ether–petroleum) (Found: C, 62.7; H, 7.4. $C_{14}H_{20}O_5$ requires C, 62.7; H, 7.5%); $\nu_{max.}$ 1 750, 1 720, 1 265, and 1 110 cm^{-1}; δ_H (100 MHz) 0.90 (3 H, s, 3a-Me), 1.01 (3 H, d, *J* 7 Hz, 3-Me), 1.81—3.00 (6 H, m, 2-H_2, 3-H, 4-H_2, and 6α-H), 3.29 (1 H, m, 6β-H), 3.22 (3 H, s, 7-OMe), 3.50 (1 H, dd, *J* 6 and 11 Hz, 7-H), and 3.82 (3 H, s, CO_2Me); δ_C (25.1 MHz) 12.9 (3-Me), 18.8 (3a-Me), 34.3 (C-3), 42.6 (C-2 or C-4), 43.2 (C-2 or C-4), 46.2 (C-6), 47.8 (C-3a), 52.1 (7-OMe), 58.4 (CO_2Me), 66.8 (C-7a), 77.5 (C-7), 168.7 (CO_2), 207.3 (C-5), and 207.6 (C-1); *m/z* (e.i.) 268 (M^+, 0.3%), 169 (62), 168 (59), 137 (100), 136 (37), 135 (30), 100 (35), 69 (45), and 57 (37) (Found: M^+, 268.1346. $C_{14}H_{20}O_5$ requires 268.1310).

(3R*,3aS*,7aR*)- *and* (3S*,3aS*,7aR*)-*Methyl* 2,3,3a,7a-*Tetrahydro*-3,3a-*dimethyl*-1,5(4H)-*dioxoindene*-7a-*carboxylate* (**17**) *and* (**18**).—A solution of the oxo ester (**13**) (3.5 mg, 20.8 mmol) and the diene (**12**) (7.18 g, 41.7 mmol) in dry methylene dichloride (4 ml) was kept at a pressure of 15 kBar for 4 days at room temperature (see ref. 48 for details). To this was added methylene dichloride (75 ml) and camphorsulphonic acid (CSA) (50 mg) and the solution stirred at room temperature for 2 h. Methylene dichloride (200 ml), ether (100 ml), and aqueous sodium hydrogen carbonate (50 ml) were added and the organic extract was washed with brine (50 ml), dried, and the solvent evaporated to give a dark brown oil. Chromatography (ethyl acetate–petroleum 1:1) gave the enones (**17**) and (**18**) as a 4:1 mixture respectively (3.5 g, 71% total).

The enone (**18**), m.p. 58—59 °C (from ethyl acetate–petroleum) (Found: C, 65.9; H, 6.7. $C_{13}H_{16}O_4$ requires C, 66.1; H, 6.8%); $\nu_{max.}$ 1 760s, 1 740s, 1 730s, 1 695s (α,β-unsaturated ketone), and 1 240s cm^{-1}; $\lambda_{max.}$ 224 (ε 4 900 dm^3 mol^{-1} cm^{-1}) and 242 nm (3 000); δ_H (360 MHz) 0.97 (3 H, d, *J* 6.9 Hz, 3-Me), 1.04 (3 H, s, 3a-Me), 2.09 (1 H, dd, *J* 10.9 and 19.4 Hz, poss. 2α-H), 2.16 and 2.21 (2 H, 2 × d, *J* 15.4 Hz, 4-H_2), 2.60 (1 H, ddq, *J* 6.9, 9.6, and 10.9 Hz, 3-H), 2.79 (1 H, dd, *J* 9.6 and 19.4 Hz, poss. 2β-H), 3.70 (3 H, s, CO_2Me), 6.07 (1 H, d, *J* 10 Hz, 6-H), and 6.82 (1 H, d, *J* 10 Hz, 7-H); δ_C (90.5 MHz) 12.4 (13-Me), 20.6 (3a-Me), 37.1 (C-3), 42.5 (C-2 or C-4), 44.5 (C-2 or C-4), 49.5 (C-3a), 52.7 (CO_2Me), 67.2 (C-7a), 129.0 (C-6), 143.2 (C-7), 169.5 (CO_2), 196.8 (C-5), and 209.4 (C-1); *m/z* (e.i.) 236 (M^+, 7%), 135 (100), 107 (11), 91 (21), 79 (54), 77 (26), 69 (15), 59 (18), and 43 (34) (Found: M^+, 236.1042. $C_{13}H_{16}O_4$ requires *M*, 236.1049).

(2S*,3R*)-*Methyl*-2-(trans-4-*Methoxy*-2-*oxobut*-3-*enyl*)-2,3-*dimethyl*-5-*oxocyclopentane*-1-*carboxylate* (**22**).—Methyllithium (2.80 mmol, 1.4M solution in ether) was added over 5 min to a solution of the diene (**21**) (507 mg, 2.94 mmol) in dry DME (80 ml) under argon at −50 °C. The solution was stirred at −50 °C for 80 min, cooled to −90 °C and rapidly added to a stirred solution of the oxoester (**13**) (336 mg, 2 mmol) in dry

THF (80 ml). After being warmed to −78 °C the solution was stirred at −78 °C for 4 h and −40 °C for 2 h. Aqueous disodium hydrogen orthophosphate (20 ml) was added, this was followed by extraction with methylene dichloride (250 ml). The combined extracts were dried and the solvent evaporated to give a pale brown oil (580 mg). The excess of methoxyketone, derived from diene (**21**), was removed on a high vacuum pump to give the title compound (**22**) as a viscous oil (482 mg, 90%); $\nu_{max.}$ 1 765, 1 730, 1 680, 1 645, 1 625, 1 600, 1 445, 1 260, 1 220, and 1 160 cm^{-1}; δ_H (60 MHz) 0.90—1.2 (6 H, m, 2- and 3-Me), 1.9—3.0 (6 H, m, 1-, 3 H, 4-H_2, and 1′-H_2), 3.65—3.85 (6 H, m, CO_2Me and 4′-OMe), 5.60 (0.4 H, d, *J* 12 Hz, 3′-H), 5.68 (0.6 H, d, *J* 12 Hz, 3′-H), 7.60 (0.4 H, d, *J* 12 Hz, 4′-H, and 7.65 (0.6 H, d, *J* 12 Hz, 4′-H); *m/z* (e.i.) 167 (9), 138 (130), 137 (27), 136 (14), 100 (34), 85 (100), 83 (14), and 69 (32) (Found: M^+ − MeOH, 236.1034. $C_{13}H_{16}O_4$ requires *M* − MeOH, 236.1049).

(3R*,3aS*)-*Methyl* 2,3,3a,6,7,7a-*Hexahydro*-7-*hydroxy*-3,3a-*dimethyl*-1,5(4H)-*dioxoindene*-7a-*carboxylate* (**24a,b**) *and* (**25a,b**).—Dilute hydrochloric acid (0.02M; 10 ml) was added to a solution of the crude enone (**22**) (482 mg, 1.80 mmol) in THF (10 ml) with stirring at room temperature. After 3 h, this was extracted with methylene dichloride (3 × 50 ml) and the combined extracts were dried, and the solvent evaporated to give the title compounds (**24a,b**) and (**25a,b**) as a brown, viscous oil (426 mg, 93%); δ_H (60 MHz) includes 1.02 (3 H, s, 3a-Me), 1.05 (3 H, d, *J* 6 Hz, 3-Me), 3.74, 3.76, and 3.80 (3 H, 3 × s, CO_2Me), 4.17 (0.6 H, dd, *J* 5 and 11 Hz, 7-H), and 4.70 (0.4 H, m, 7-H).

(3R*,3aS*,7aR*)-*Methyl* 2,3,3a,7a-*Tetrahydro*-3,3a-*dimethyl*-1,5(4H)-*dioxoindene*-7a-*carboxylate* (**17**).—To the β-hydroxyketones (**24**) and (**25**) (1.61 g, 6.34 mmol) in methylene dichloride (10 ml) at −10 °C was added *N,N*-di-isopropylethylamine (2 ml, 1.48 g, 11.5 mmol), methanesulphonyl chloride (2 ml, 2.96 g, 26 mmol) and phosphorus oxychloride (0.8 ml, 1.33 g, 8.7 mmol). After 3 h, THF (15 ml) and aqueous sodium hydrogen carbonate (5 ml) were added, this was followed by extraction with methylene dichloride (3 × 70 ml). The combined extracts were dried and the solvent evaporated to give a brown oil. Chromatography (ethyl acetate–chloroform 1:1) gave the enone (**17**) (1.0 g, 67%).

(3R*,3aS*,7aR*)-*Methyl* 2,3,3a,4,5,7a-*Hexahydro*-1,5-*dihydroxy*-3,3a-*dimethylindene*-7a-*carboxylate* (**26**).—To a solution of the enone (**17**) (640 mg, 2.71 mmol) in methanol (50 ml) at room temperature was added cerium trichloride heptahydrate (1.02 g, 2.72 mmol) in methanol (10 ml) rapidly followed by sodium borohydride (280 mg, 7 mmol) over 3 min. Water (10 ml) was added and the solution was extracted with methylene dichloride (6 × 100 ml). The combined extracts were washed with aqueous sodium hydrogen carbonate (10 ml), dried, and the solvent evaporated to give the title compound (**26**) as a yellow oil (610 mg, 94%). A small sample of the major diastereoisomer (55% of the mixture) was obtained by chromatography (ethyl acetate–light petroleum 1:1); $\nu_{max.}$ 3 400, 1 710, 1 650, 1 250, and 1 050 cm^{-1}; δ_H (360 MHz) 0.70 (3 H, s, 3a-Me), 0.79 (3 H, d, *J* 7 Hz, 3-H), 1.5—2.3 (5 H, m, 2-H_2, 3-H, and 4-H_2), 3.64 (3 H, s, CO_2Me), 4.20 (1 H, br t, *J* 8 Hz, 1-H), 4.83 (1 H, t, *J* 8 Hz, 5-H), 5.72 (1 H, d, *J* 11 Hz, 7-H), and 5.92 (1 H, m, 6-H); *m/z* (e.i.) 240 (M^+, 0.4%), 208 (24), 151 (100), 137 (49), 119 (31), 107 (71), 96 (65), 59 (55), and 41 (37) (Found: M^+, 240.1375. $C_{13}H_{20}O_4$ requires *M*, 240.1361).

(3R*,3aS*,7aR*)-*Methyl* 2,3,3a,4,5,7a-*Hexahydro*-3,3a-*dimethyl*-1,5-*bis*-[2-(*trimethylsilyl*)*ethoxymethoxy*]*indene*-7a-*carboxylate* (**27**). 2-(Trimethylsilyl)ethoxymethoxy chloride (900 mg, 5.40 mmol) and *N,N*-di-isopropylethylamine (1.05 g, 1.4 ml, 8.1 mmol) was added to a solution of the diol (**26**) (601 mg, 2.54 mmol) in methylene dichloride (15 ml) under nitrogen and the mixture heated under reflux for 6 h. After being cooled to room temperature, the reaction was poured into ether–methylene dichloride (1:1, 400 ml). The organic extract was washed with dilute hydrochloric acid (2 × 20 ml), water (40 ml), dried, and the solvent evaporated to give the title compound (**27**) as an orange oil (1.27 g, 100%); $\nu_{max.}$ 1 720, 1 250, 1 100, 1 060, 1 040, 865, and 840 cm^{-1}; δ_H (60 MHz) major diastereoisomer 0.03 (18 H, s, 2 × $SiMe_3$), 0.65—1.0 (10 H, m, 3-Me, 3a-Me, and $TMSCH_2CH_2$), 1.6—2.5 (5 H, m, 2-H_2, 3-H, and 4-H_2), 3.4—3.8 (4 H m, $TMSCH_2CH_2$), 3.67 (3 H, s, CO_2Me), 4.20 (1 H, t, *J* 9 Hz, 1-H), 4.70 (2 H, br s, 1-OCH_2), 4.75 (2 H, br s, 5-OCH_2, 4.88 (1 H, m, 5-H), 5.75 (1 H, d, J 11 Hz, 7-H), and 5.95 (1 H, m, 6-H); *m/z* (c.i., NH_3) 518 (MNH_4^+, 23%), 442 (52), 427 (99), 325 (32), 295 (88), 205 (25), 143 (36), 90 (100), and 73 (51).

(3R*,3aS*,7aS*)-2,3,3a,4,5,7a-*Hexahydro*-3,3a-*dimethyl*-1,5-*bis*-[2-(*trimethylsilyl*)*ethoxymethoxy*]*inden*-7a-*ylmethanol* (**28**).—Lithium aluminium hydride (2.5 mmol; 0.5M solution in ether was added to a solution of the ester (**27**) (1.27 g, 2.54 mmol) in dry THF (50 ml) under nitrogen and the solution stirred at room temperature for 30 min. The solution was cooled to 0 °C and water (5 ml) was added dropwise over 5 min followed by dilute hydrochloric acid (20 ml). This was extracted with methylene dichloride (2 × 125 ml) and the combined extracts were washed with water (50 ml), dried, and the solvent evaporated to give the title compound (**28**) as pale orange oil (1.14 g, 91%); $\nu_{max.}$ 3 480 (br, OH), 1 250m, 1 105m, 1 060vs, 865s, and 840s cm^{-1}; δ_H (60 MHz) major diastereoisomers 0.03 (18 H, s, $SiMe_3$), 0.65—1.10 (7 H, m, 3-Me and $TMSCH_2$), 0.78 (3 H, s, 3a-Me), 1.4—2.3 (6 H, m, OH, 2-H_2, 3-H, and 4-H_2), 3.40—3.75 (4 H, m, $TMSCH_2CH_2$), 3.55 (2 H, br s, 7a-CH_2), 4.00 (1 H, br t, *J* 8 Hz, 1-H), 4.20 (1 H, br t, *J* 9 Hz, 5-OH), 4.66 (2 H, s, 1-OCH_2), 4.74 (2 H, s, 5-OCH_2), 5.80 (1 H, d, *J* 11 Hz, 7-H), and 6.05 (1 H, m, C-H).

(3R*,3aS*,7aS*)-2,3,3a,4,5,7a-*Hexahydro*-3,3a-*dimethyl*-1,5-*bis*-[2-(*trimethylsilyl*)*ethoxymethoxy*]*inden*-7a-*ylmethyl Toluene*-p-*sulphonate* (**29**).—Toluene-*p*-sulphonyl chloride (1.83 g, 9.60 mmol) and 4-dimethylaminopyridine (283 mg, 2.32 mmol, 1 equiv.) were added to a solution of the alcohol (**28**) (1.14 g, 2.32 mmol) in pyridine (6 ml) and the reaction stirred at room temperature for 24 h. To this was then added methylene dichloride (25 ml) followed, after cooling to 0 °C by 3-dimethylaminopropylamine (1 ml, 1.44 g, 14 mmol) (to react with the excess of toluene-*p*-sulphonyl chloride). After 5 min the reaction was poured into methylene dichloride–water (3:1, 200 ml). The organic extract was washed with dilute hydrochloric acid (2 × 100 ml), brine (40 ml), water (40 ml), then dried and the solvent evaporated to give an opaque, colourless oil (1.61 g). Chromatography (light petroleum–methylene dichloride–ether, 7:2:1) gave the title compound (**29**) as a colourless oil (1.27 g, 88%); $\nu_{max.}$ 1 600, 1 370, 1 250, 1 195, 1 180, 1 105, 1 060, 1 040, 980, 955, 870, and 840 cm^{-1}; δ_H (60 MHz) major diastereoisomer 0.04 (18 H, s, 2 × $SiMe_3$), 0.72 (3 H, s, 3a-Me), 0.83 (3 H, d, *J* 7 Hz, 3-Me), 0.90 (4 H, 2 × br t, *J* 8 Hz, $TMSCH_2CH_2$), 1.3—2.3 (5 H, m, 2-H_2, 3-H, and 4-H_2), 2.42 (3 H, s, ArMe), 3.4—3.85 (4 H, 2 × br t, *J* 8 Hz, $TMSCH_2CH_2$), 3.9—4.3 (2 H, m, 1- and 5-H), 3.97 (2 H, br s, 7a-CH_2), 4.59 (2 H, s, 1-OCH_2), 4.70 (2 H, s, 5-OCH_2), 5.57 (1 H, br d, *J* 11 Hz, 7-H), 5.85 (1 H, m, 6-H), 7.28 (2 H, d, *J* 8 Hz, 3′- and 5′-ArH), and 7.78 (2 H, d, *J* 8 Hz, 2′- and 6′-ArH); *m/z* (c.i., NH_3) 644 (MNH_4^+, 3%), 473 (86), 317 (67), 262 (69), 164 (42), 159 (69), 91 (66), 90 (100), and 73 (58) (Found: MNH_4^+, 644.3422. $C_{31}H_{58}NO_7SSi_2$ requires MNH_4, 644.3472).

(3R*,3aS*,7aS*)-2,3,3a,4,5,7a-*Hexahydro*-3,3a,7a-*trimethyl*-1,5-*bis*-[2-(*trimethylsilyl*)*ethoxymethoxy*]*indene* (**30**).—(i) *Lithium aluminium hydride.* Lithium aluminium hydride (4 mmol; 0.5M in ether) was added to a solution of the toluene-*p*-sulphonate (**29**) (145 mg, 0.23 mmol) in dry THF (10 ml) under nitrogen, the solution warmed to 40 °C, and the ether distilled. The reaction mixture was heated under reflux for 14 h, and after cooling to 0 °C, water (5 ml) was added dropwise over 10 min. After being acidified with dilute hydrochloric acid (5 ml), the solution was extracted with ether (2 × 30 ml) and the combined extracts were washed with aqueous sodium hydrogen carbonate (10 ml) and water (10 ml), dried, and the solvent evaporated to give a colourless oil. Chromatography (light petroleum–methylene dichloride–ether 15:4:1→10:4:6) gave the alcohol (**28**) (55 mg, 50%) and the title compound (**30**) as a colourless oil (11 mg, 10%); $\nu_{max.}$ 1 255, 1 110, 1 065, 1 040, 950, 930, 870, and 850 cm^{-1}; δ_H (360 MHz) 0.03 (18 H, s, 2 × $SiMe_3$), 0.72 (3 H, s, 3a-Me), 0.87 (3 H, d, *J* 7 Hz, 3-Me), 0.94 (4 H, br t, *J* 7.5 Hz, $TMSCH_2CH_2$), 1.02 (3 H, s, 7a-Me), 1.33 (1 H, dd, *J* 10.3 and 13.1 Hz, 4-H), 1.64 (2 H, m, 2-H_2), 1.84 (1 H, br dd, *J* 6.8 and 13.1 Hz, 4-H), 2.20 (1 H, m, includes *J* 7 Hz, C-H), 3.54—3.73 (4 H, m, $TMSCH_2CH_2$), 3.97 (1 H, br dd, *J* 8.3 and 8.4 Hz, 1-H), 4.17 (1 H, m, 5-H), 4.68 (2 H, 2 × d, *J* 17 Hz, 3-OCH_2), 4.76 (2 H, 2 × d, *J* 17 Hz, 5-OCH_2), 5.62 (1 H, br d, *J* 10.5 Hz, 7-H), and 5.83 (1 H, dd, *J* 1.7 and 10.5 Hz, 6-H); *m/z* (c.i., NH_3) 474 (*M*NH_4^+, 9%), 251 (33), 195 (18), 163 (67), 161 (37), 143 (13), 91 (14), 90 (100), and 73 (44) (Found: *M*NH_4^+, 474.3993. $C_{24}H_{52}NO_4Si_2$ requires *M*NH_4, 474.3434).

(ii) *Lithium triethylborohydride.* Lithium triethylborohydride (2 mmol; 1M solution in THF) was added to a solution of the toluene-*p*-sulphonate (**29**) (145 mg) in dry THF (5 ml) under argon and the reaction mixture heated under reflux for 14 h. Water (10 ml) was added dropwise over 5 min followed by dilute hydrochloric acid (5 ml), ether (40 ml), and methylene dichloride (20 ml). The organic extract was washed with aqueous sodium hydrogen carbonate (10 ml), water (10 ml), dried, and the solvent evaporated to give a pungent smelling oil. Chromatography gave the alkene (**30**) (15 mg, 14%), identical with that previously isolated, and the alcohol (**28**) (91 mg, 84%).

(iii) *Sodium iodide and zinc.* Sodium iodide (2 g, 13.4 mmol) and zinc (1.75 g, 26.7 mmol) was added to a solution of the toluene-*p*-sulphonate (**29**) (1.67 g, 2.67 mmol) in hexamethylphosphoramide (27 ml) under argon. This was heated to 110 °C for 3 days and then poured into petroleum–ether (7:3, 200 ml). This mixture was washed with saturated lithium chloride solution (4 × 70 ml) and aqueous sodium hydrogen carbonate (40 ml), dried, and the solvent evaporated to give an oil contaminated with hexamethylphosphoramide. Chromatography (light petroleum–ether, 3:1) gave the alkene (**30**) (81 mg, 66%).

(3R*,3aS*,7aS*)-2,3,3a,4,5,7a-*Hexahydro*-3,3a,7a-*trimethylindene*-1,5-*diol* (**31**).—Tetrabutylammonium fluoride (10 mmol) was added to a solution of the alkene (**30**) (650 mg, 1.42 mmol) in hexamethylphosphoramide (3 ml) under nitrogen and the solution heated at 85 °C for 24 h. Water (80 mg) was added and the mixture was directly chromatographed (ethyl acetate–light petroleum–chloroform, 5:4:1) to give the title compound (**31**) as a red oil (127 mg, 46%); $\nu_{max.}$ 3 360, 1 450, 1 265, 1 060, and 1 040 cm^{-1}; δ_H (60 MHz) 0.70 (3 H, s, 3a-Me), 0.85 (3 H, d, *J* 7 Hz, 3-Me), 1.00 (3 H, s, 7a-Me), 1.25—2.25 (7 H, m, 2-H_3, 3-H, 4-H_2, and 2 × OH), 3.98 (1 H, m, 1-H), 4.25 (1 H, m, 5-H), 5.68 (1 H, m, 7-H), and 5.80 (1 H, m, 6-H); *m/z* (c.i., NH_3) 196 (M^+, 6%), 179 (97), 161 (100), 135 (11), 119 (22), 107 (84), 95 (16), 91 (35), and 41 (14).

(3R*,3aS*,7aS*)-2,3,3a,7a-*Tetrahydro*-3,3a,7a-*trimethylindene*-1,5(4H)-*dione* (**32**).—Powdered molecular sieves (1 g) and pyridinium chlorochromate (1 g, 4.6 mmol) was added to a solution of the diol (**31**) (127 mg, 0.65 mmol) in dry methylene dichloride (20 ml) with stirring. After 4 h, the solution was filtered through florisil and the residue washed with petroleum–ether (1:1, 100 ml). The combined filtrate was evaporated to give a yellow solid. Chromatography (ethyl acetate–light petroleum, 1:1) gave the title compound (**32**) as a white, crystalline solid (68 mg, 54%), m.p. 68—70 °C (ethyl acetate–light petroleum); $\nu_{max.}$ 1 750 and 1 690 cm^{-1}; δ_H (360 MHz) 0.90 (3 H, s, 3a-Me), 1.02 (3 H, d, *J* 7 Hz, 3-Me), 1.18 (3 H, s, 7a-Me), 2.00 (1 H, dd, *J* 11.9 and 19 Hz, 2β-H), 2.32 (1 H, ddq, *J* 7, 8.2 and 11.9 Hz, 3-H), 2.33 (1 H, d, *J* 17 Hz, 4α-H), 2.49 (1 H, dd, *J* 8.2 and 19 Hz, 2α-H), 2.57 (1 H, d, *J* 17 Hz, 4β-H), 6.02 (1 H, d, *J* 10 Hz, 6-H), and 6.32 (1 H, d, *J* 10 Hz, 7-H); *m/z* (e.i.) 192 (M^+, 3%), 123 (100), 107 (60), 94 (62), 91 (39), 79 (81), 69 (81), 53 (22), and 41 (79) (Found: M^+, 192.1159. $C_{12}H_{16}O_2$ requires *M*, 192.1150).

(4R*,4aS*,7R*,7aS*)-4,4a,6,7a,8-*Hexahydro*-4,4a,7,7a-*tetramethylindeno*[5,6-b]*furan*-3(2H),5-*dione*.—Methyl lithium (3.2 mmol; 1.6M in ether) was added to a solution of powdered copper iodide (304 mg, 1.6 mmol) in dry ether (5 ml) under argon at 0 °C with rapid stirring. After 45 min the solution was cooled to −25 °C and the enone (**32**) (70 mg, 0.36 mmol) in dry ether (3 ml) was added dropwise over 10 min. After 1 h the solution was cooled to −55 °C and chloroacetyl chloride (0.54 g, 4.8 mmol) in ether (3.5 ml) was added. The mixture was slowly warmed to −10 °C over 1 h, stirred at room temperature for 20 min and then poured into ice–0.88 ammonia (3:1, 5 g). The aqueous layer was immediately extracted with ether (3 × 30 ml) and the combined extracts were washed with dilute ammonia (10 ml) and brine (10 ml), dried, and the solvent evaporated to give a solid. Chromatography (light petroleum–ethyl acetate, 7:3, 1:1) gave the title compound (**33**) as a yellow oil as the only product (81 mg, 90%); $\nu_{max.}$ 1 740, 1 700, 1 645, 1 435, 1 140, and 1 000 cm^{-1}; δ_H (360 MHz), 0.89 (3 H, s, 7a-Me), 1.04 (3 H, s, 4a-Me), 1.91 (3 H, d, *J* 7 Hz, 7-Me), 1.17 (3 H, d, *J* 8 Hz, 4-Me), 1.94 (1 H, dd, *J* 12 and 19 Hz, 6β-H), 2.19 (1 H, ddq, *J* 7, 8, and 12 Hz, 7-H), 2.27 (1 H, d, *J* 17 Hz, 8-H), 2.41 (1 H, dd, *J* 8 and 19 Hz, 2α-H), 2.52 (1 H, q, *J* 8 Hz, 4-H), 2.67 (1 H, d, *J* 17 Hz, 8-H), and 4.48 (2 H, 2 × d, *J* 17 Hz, 2-H_2); δ_C (90.5 MHz) 13.6, 18.0, 19.2, and 19.8 (4-Me, 4a-Me, 7-Me, and 7a-Me), 31.3 (C-7), 34.2 (C-8), 34.8 (C-4), 44.2 (C-6 or C-7a), 45.5 (C-6 or C-7a), 56.0 (C-4a), 74.6 (C-2), 113.9 (C-3a), 185.6 (C-8a), 200.7 (C-3), and 213.8 (C-5); *m/z* (c.i., NH_3), 249 (*M*H^+, 27%), 248 (M^+, 10), 233 (9), 135 (9), 125 (100), 109(97), 81 (8), and 43 (13) (Found: M^+, 248.1413. $C_{15}H_2O_3$ requires *M*, 248.1412).

(4S*,4aS*,7R*,7aS*)-4,4a,6,7,7a,8-*Hexahydro*-4,4a,7,7a-*tetramethylindeno*[5,6-b]*furan*-5-*one* (4-epi-*Pinguisone*) (**34**).—9-Borabicyclononane (0.3 mmol; 0.5M solution in THF) was added to a solution of the enone (**33**) (75 mg, 0.3 mmol) in dry THF (2 ml) under argon at 0 °C with stirring. After 1 h, t.l.c. analysis revealed the presence of two products together with starting material. Further 9-BBN (0.2 mmol) was added in order to achieve complete consumption of the enone (**33**). Methanol (0.3 ml) was added, the solvent evaporated, and ethanolamine (30 mg, 0.5 mmol) in pentane (5 ml) was added. The precipitate was filtered through florisil and residue washed with pentane (50 ml). The combined filtrate was evaporated to yield a colourless oil. Flash chromatography (petroleum–ether–methylene dichloride, 8:1:1) as eluant gave the title compound (**34**) as a white solid (36 mg, 50%), m.p. 58—59 °C (pentane) (Found: C, 77.0; H, 8.6. $C_{15}H_{20}O_2$ requires C, 77.55; H, 8.7%); $\nu_{max.}$ 1 740, 1 455, 1 410, 1 385, 1 375, 1 115, and 901m cm^{-1}; $\lambda_{max.}$ 227 nm (ε 5 200 dm^3 mol^{-1} cm^{-1}); δ_H (360 MHz) 0.86 (3 H, s, 7a-Me), 0.98 (3 H, d, 6.6 Hz, 7-Me), 1.05 (3 H, s, 4a-Me), 1.16 (3 H, d, *J* 8.4 Hz, 4-Me), 1.94 (1 H, dd, *J* 10.5 and 18.8 Hz, 6β-H),

2.20 (1 H, ddq, *J* 6.6, 8.9, and 10.5 Hz, 7-H), 2.33 (1 H, br d, *J* 17.3 Hz, 8-H), 2.37 (1 H, dd, *J* 8.9 and 18.8 Hz, 6α-H), 2.57 (1 H, dd, *J* 1.8 and 8.4 Hz, 4-H), 2.82 (1 H, d, *J* 17.3 Hz, 8-H), 6.23 (1 H, d, *J* 1.8 Hz, 3-H), and 7.29 (1 H, d, *J* 1.8 Hz, 2-H); δ_C (90.5 MHz) 13.8, 19.4, 19.9, and 21.1 (4-, 4a-, 7-, and 7a-Me), 28.6 (C-7), 33.2 (C-8), 37.2 (C-4), 44.5 (C-6 or C-7a), 46.1 (C-6 or C-7a), 56.6 (C-4a), 109.7 (C-3), 118.4 (C-3a), 141.1 (C-2), 147.0 (C-8a), and 212.0 (C-5); *m/z* (c.i., NH_3), 232 (M^+, 7%), 125 (5), 109 (9), 108 (100), 107 (7), 91 (4), 79 (8), and 41 (6) (Found: M^+, 232.1478. $C_{15}H_{20}O_2$ requires *M*, 232.1463).

Further elution gave (4*R**,4a*S**,7*R**,7a*S**)-4,4a,6,7,7a,8-hexahydro-5-hydroxy-4,4a,7,7a-tetramethyl-5*H*-indeno[5,6-*b*]furan (4-*epi*-pinguisanol) (**35**) as a colourless oil (14 mg, 20%); $\nu_{max.}$ 3 460, 1 440, 1 380, 1 205, 1 120, 1 040, and 1 030 cm^{-1}; δ_H (360 MHz) 0.98 (6 H, s, 4a- and 7a-Me), 1.07 (3 H, d, *J* 7 Hz, 7-Me), 1.41 (3 H, d, *J* 8 Hz, 4-Me), 1.59 (1 H, br, OH), 1.7 (1 H, m, 7-H), 2.11 and 2.16 (2 H, m, 6-H_2), 2.47 (1 H, d, *J* 17 Hz, 8-H), 2.58 (1 H, br q, *J* 8 Hz, 4-H), 2.94 (1 H, br d, *J* 17 Hz, 8-H), 4.15 (1 H, d, *J* 3.8 Hz, 5-H), 6.23 (1 H, d, *J* 1.8 Hz, 3-H), and 7.25 (1 H, d, *J* 1.8 Hz, 2-H); *m/z* (e.i.) 234 (M^+, 2%), 147 (7), 146 (13), 109 (19), 108 (100), 107 (7), 91 (6), 79 (9), and 77 (7) (Found: M^+, 234.1629. $C_{15}H_{22}O_2$ requires *M*, 234.1620).

Crystallographic Measurements.—The single crystal structure was obtained by *X*-ray diffraction on a specimen grown in ethyl acetate–pentane with approximate dimensions of 0.2 × 0.4 × 0.8 mm. The crystal was mounted in air with epoxy at ambient temperature. Data was collected on a fully automated Enraf–Nonius CAD4 four circle, kapp geometry diffractometer using graphite-monochromated Cu-K_α (λ = 1.5418 Å) radiation at 50 kV/20 ma, ω scan (ω scan angle = 0.8 + 14Tan [θ]°) up to a maximum 2θ of 115°. A total of 1 695 symmetry independent reflections were collected of which 1 584 were considered observed at the level $I > 3\sigma(I)$. No discernable sample decay was noted as monitored by three check reflections measured after every 60 minute data collection interval. Corrections were made for Lorentz and polarisation factors but not for absorption.

The unit cell parameters are a = 11.568(2) Å, b = 7.905(3) Å, c = 13.604(3) Å, $\alpha = \gamma = 90°$, β = 92.062(2)° and V = 1 243(1) $Å^3$ in the centrosymmetric, monoclinic space group $P2_1/c$ (Z = 4), D_c = 1.262 g cm^{-3}, μ = 7.325 cm^{-1}. The structure was solved by the application of direct methods using the multiple tangent approach of MULTAN(1), a series of computer programs running on a PDP 11/60 computer. All data reduction, least squares, electron density syntheses and other related computations were carried out by SDP(2) with scattering factor coefficients of Cromer and Waber (3). The solution was refined using full matrix least squares minimising the function of $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F_o)^2$ to an unweighted residual index (R) of 0.051 and weighted index (R_w) of 0.099 (R-factor = $\Sigma||F_o| - ||F_c||/\Sigma|F_o|$). Non-hydrogen atoms were refined anisotropically while hydrogen atoms were assigned equivalent isotropic temperature factors of the atoms to which they were bound and refined for positional parameter variation only. Initial hydrogen co-ordinates were calculated at idealised positions. Computer generated pictures are those of ORTEP(4). Thermal parameters are available on request from the Cambridge Crystallographic Data Centre.*

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* See 'Instructions for Authors (1988),' para. 5.6.3, *J. Chem. Soc., Perkin Trans. 1*, Issue 1.

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