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THE STRUCTURE AND RELATIVE CONFIGURATION OF THE DECIPIENE DITERPENES

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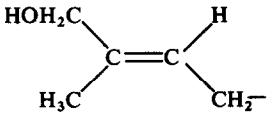
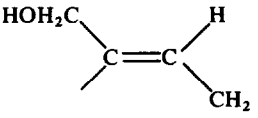
Abstract—The structures and relative configuration of three decipiene diterpenes from *Eremophila decipiens* have been established by degradation studies. These diterpenes possess the new tricyclic decipiane skeleton based on the tricyclo [5,3,1,$0^{5,11}$] undecane ring system.

The unusual biosynthetic processes for polyterpenes in *Eremophila*, typified by diterpenes such as eremolactone and its congeners[1-3] and sesquiterpenes like freelingyne[4] point to the need to extend the phytochemical study of this large genus. *Eremophila decipiens* is widely distributed in Southern Western Australia and is cultivated for its floral character. We find its surface coating consists of a complex mixture of diterpenes including the triol (**1**), the hydroxy acid (**2**) and the dihydroxy acid (**3**), all of which possess a new tricyclic skeleton which we have named decipiane[a] This skeleton resembles eremolactone in that it may be regarded as an isoprenologue of a sesquiterpene which remains to be discovered.

Extensive chromatography of the neutral fraction provided the triol (**1**) whose NMR spectra revealed the presence of a tertiary hydroxymethyl, a secondary Me and two olefinic protons. The latter were identified as the functions **A** and **B** by NMDR studies.



A



B

The NMR spectrum also revealed a deshielded tertiary methine proton as a broadened doublet at δ 3.17 (J 9Hz) coupled to a proton at δ 2.72, (ddd) subsequently assigned to the cyclobutyl protons at C-16 and C-17 respectively.

The presence of two primary allylic alcohols was confirmed by Pd-catalysed hydrogenolysis and hydrogenation of the acetylation product of the triol which gave the monoacetate (**4**) retaining the olefinic proton of group **B**.

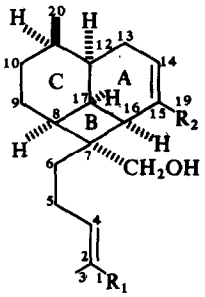
The acetate was converted to the parent hydrocarbon by the conventional sequence **5** → **6** → **7** → **8**. The hydrocarbon, $C_{20}H_{36}$, is saturated and therefore tricarbocyclic.

The acidic fraction of the plant extract was chromatographed on SiO_2 and gave the hydroxy acid (**2**) and the dihydroxy acid (**3**) in crystalline form. The latter was converted to the triol (**1**) by methylation and reduction with AlH_3 and the position of the carboxyl group was evident from the appearance of the broad triplet at δ 7.13 (J 7Hz) for the olefinic proton in group **A**. The structure of the hydroxy acid (**2**) was readily assigned since its NMR spectrum showed a similar olefinic proton signal together with resonances for a tertiary hydroxymethyl and two olefinic Me groups. Correlation with the triol was achieved by methylation and AlH_3 reduction to the diol (**9**) which, after acetylation and Pd-catalysed hydrogenolysis and hydrogenation gave the monoacetate (**4**) described above.

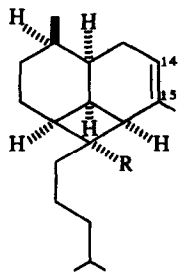
The triol and the related hydroxy acids comprise only a small part of the resin and although no other substances were separated in a pure state, chromatographic and spectroscopic indications suggested an array of compounds which appeared to arise by permutation of the oxidation level of the pendant groups in **1**. Simplification of the neutral fraction by hydrogenolysis-hydrogenation was an attractive approach since this would convert pendant allylic groups to methyls and eliminate stereochemical complications in the side chain. The best procedure for this purpose involved acetylation of the crude neutral extract followed by reduction with Li–NH_3 and then Pd–catalysed hydrogenation. Chromatography of the product thus formed on alumina gave useful quantities of decipi-14-ene (**7**), the alcohol (**5**) and a hydroxy ether (**10**). The NMR spectrum of this ether showed signals for two secondary Me's and an olefin Me and its associated proton whose appearance suggested derivation from group **B**. A doublet at δ 3.48 (J 6Hz) was assigned to the secondary hydroxymethyl and an AB quartet with further coupling to the low field proton indicated a primary ether link. Further spectral study was facilitated by reductive removal of the primary OH by tosylation and treatment with LAH. Application of the shift reagent Eu $(dpm)_3$ to the desoxy compound (**12**) obtained identified the secondary ether terminus adjoining an isopropyl group on one side and a methylene on the other. Correlation with the triol (**1**) was achieved by way of the olefin ether (**13**) prepared by t-BuOK elimination of the tosylate derivative of the hydroxy ether. Hydrogenolysis of the allylic ether (**13**) with Li-EtNH_2 followed by hydrogenation of the olefin mixture and acetylation gave the acetate (**4**) identical with the sample derived from the triol (**1**).

Two lines of evidence indicate that the ether is in an unstrained ring system. Firstly, the geminal coupling for the C-18 protons is 11.5 Hz, which lies near the midpoint for such unstrained systems.[5] Further when

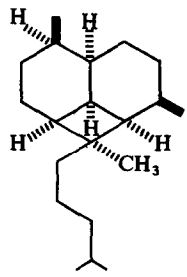
[a] A preliminary report of this work appeared in Tetrahedron Letters, 1775 (1975) and the results of an X-ray crystallographic analysis on the hydroxy acid (**2**) has been published (Ref. 10).



	R_1	R_2
1	CH_2OH	CH_2OH
2	CO_2H	CH_3
3	CO_2H	CH_2OH
9	CH_2OH	CH_3



4 R = CH_2OAc
5 R = CH_2OH
6 R = CHO
7 R = CH_3



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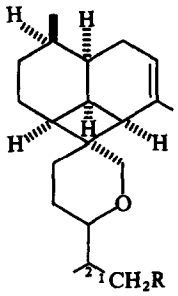
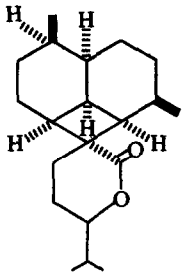


10 R = OH
11 R = OTs
12 R = H
13 Δ^1



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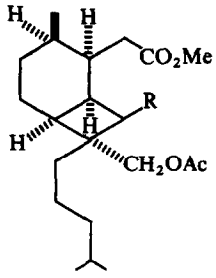
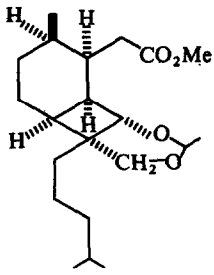


15 R = β-$COCH_3$
16 R = α-$COCH_3$
17 R = α-OH



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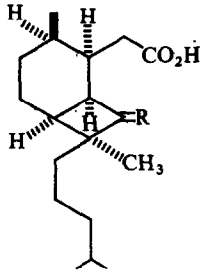
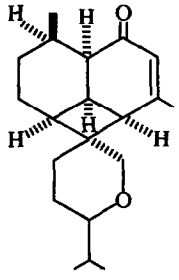


19 R = $\overset{H}{\diagdown\!\!\diagup}COCH_3$
20 R = $\overset{H}{\diagdown\!\!\diagup}OH$
21 R = O



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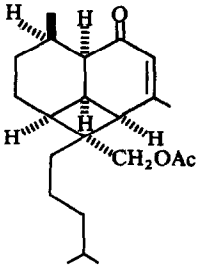
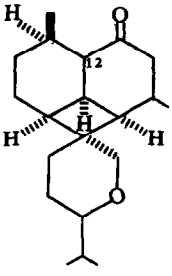
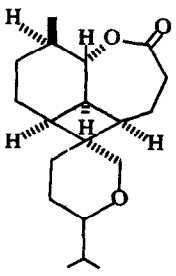


23



24 12α-H
25 12β-H



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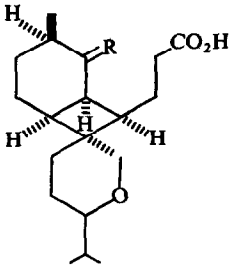
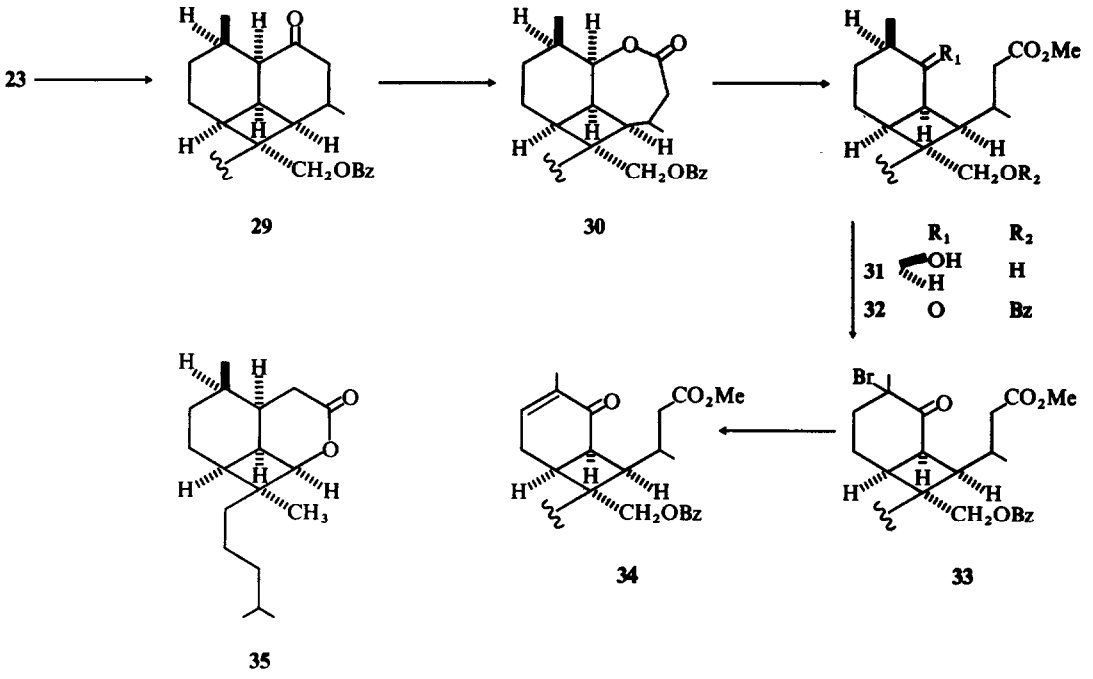


27 R = $\overset{H}{\diagdown\!\!\diagup}OH$
28 R = O

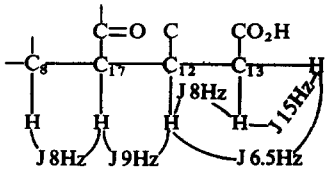


the desoxy ether (**12**) is oxidized with RuO_4 a lactone (**14**) is obtained showing ν_{max} 1720 cm^{-1}. Evidence which points to a 6-carbon side chain and hence a six or larger membered ether in **10** is obtained from examination of mass spectra. Thus the triol (**1**), acetate (**4**) and the hydrocarbons (**7** and **8**) all show significant fragments for fission of C_6–C_7.

Exploration of the tricyclic nucleus was initiated by ozonolysis of the acetate (**4**). When the ozonide was worked up with Jones reagent a keto acid, isolated as its methyl ester (**15**) was obtained. On the other hand reduction of the ozonide with Zn dust led to an epimer (**16**) which readily isomerised to **15** on exposure to acid. Bayer Villiger oxidation of the more stable epimer (**15**) gave a diacetate the NMR spectrum of which showed an acetoxymethine proton as a sharp doublet (δ 5.02, J 9Hz) which is therefore probably flanked by a quaternary carbon. The possibility that this quaternary carbon was identical with that bearing the hydroxymethyl group was strengthened by hydrolysis of this diacetate to the diol acid which was methylated to the ester (**17**) and converted to the ethylidene derivative (**18**). A similar oxidative sequence was carried out on decipi-14-ene (**7**) to yield the hydroxy acid (**20**). This was oxidized to the keto acid (**21**) which on exchange with DCl-AcOD gave a d_1-derivative. Double resonance studies on the keto acid (**21**) and its deuterated derivative located the function shown in the partial structure (**C**). The signal for the 17-H was identified by its exchange with DCl–AcOD. The identification of this substituent pattern completely delineates ring A and, taken in conjunction with a saturated side chain, C_6H_{13}, and a tertiary hydroxymethyl, leaves only CH_3–CH–C_2H_4 to be incorporated into the structure (D). Since this unit may not contain a quaternary centre the fully substituted centre adjacent to the CO in **21** necessarily carries the hydroxymethyl residue present in **1**.

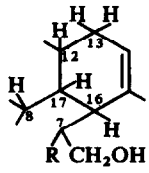
The keto acid (**21**) shows ν_{max} for a strained ketone group at 1762 cm^{-1} which lies near the bottom of the range for cyclobutanones[6] however this assignment find support on other spectral grounds. Thus the MS of the ethylidene derivative (**18**), the hydroxy acid (**20**) and the keto acid (**21**) all show base peaks for the fragment incorporating the side chain arising from fission of the 7, 8 and 16, 17 bonds which is expected if they are part of a four, but not a 5-membered ring. In addition the chemical shift for the 17-proton in all these compounds show the additional deshielding which is associated with cyclobutyl protons.[7] This strongly suggests the presence of a cyclobutane ring formed by linkage of C-7 and C-8.

Exploration of the third ring (C) was initiated by allylic oxidation of the methylene group in the acetate (**4**) and the ether (**12**). The most satisfactory procedure proved to be oxidation with CrO_3–pyridine which gave the corresponding ketones (**22** and **23**) in ~30% yield. The presence of the conjugated carbonyl group



δ – 3.81 2.44 2.83 3.11

C



D

was confirmed by spectral data and the position of CO absorption at 1655 cm^{-1} along with λ_{max} 253 nm (calc 239) for **21** requires extended overlap of the π-system attributable to a small ring. Similar anomalous spectra involving cyclobutyl overlap have been reported for verbenone and some analogues.[8] The proximity of the secondary methyl to the CO in (**21** and **22**) was apparent from the downfield shifts which it suffered on introduction of the CO (20–24Hz).

Application of the $Eu(dpm)_3$ shift reagent to **22** showed that the secondary Me reonance was deshielded to a similar extent to the α protons at C-12 and C-14 clearly implicating the adjacent C-11 as its location. Reduction of the conjugated CO in **23** with $Li–NH_3$ gave the cyclohexanone (**24**) retaining the deshielded secondary Me group. Epimerisation of this ketone occurred readily on exposure to mineral acid or Al_2O_3 chromatography to give a mixture containing 80% of the epimer (**25**). When either epimer was treated under Bayer–Villiger conditions the same lactone (**25**) was formed. The lactone readily opened on exposure to moisture to give the hydroxy acid (**27**) which was oxidized with Jones reagent to the keto acid (**28**) which showed ν_{max} 1700 cm^{-1} suggesting a 6-membered or larger ring cycloalkanone.

In contrast, the conjugated ketone (**23**) could be reduced with $Li–NH_3$ followed by benzoylation to give the saturated ketone (**29**) whose NMR spectrum still showed a deshielded secondary Me group. This ketone (**29**) under Bayer–Villiger conditions gave the lactone (**30**) without detectable epimerisation.[b] This was indicated by the appearance of the 12-H in the NMR spectrum of **30** as a narrow multiplet at δ 3.9 ($W_{\frac{1}{2}}$ 7Hz) compared to the broad multiplet ($W_{\frac{1}{2}}$ 20Hz) observed for the 12-H in **26**. Hydrolysis of **30**, followed by methylation gave the diol ester (**31**) which after rebenzoylation could be oxidized to the keto ester (**32**) which showed ν_{max} 1700 cm^{-1}.

Bromination of **32** using trimethylphenyl ammonium bromide perbromide[9] gave the monobromide (**33**) which showed a singlet at δ 1.85 for the new tertiary Me. Dehydrobromination of **33** with LiCl/DMF yielded the conjugated ketone **34** (λ_{max}: 224 nm) which showed resonances in its NMR spectrum for an olefinic Me at δ 1.82 and an olefinic proton at δ 6.64 shown by NMDR to be coupled to the olefinic Me and a vicinal methylene group (J 4Hz). This result identified the orientation of the skeleton of the decipiene diterpenes which contain the new tricyclo[5, 3, $1,0^{5,11}$] undecane ring system.

Stereochemistry. There are five stereochemical points which require elucidation in compound **1**: the stereochemistry of the side chain double bond, the AC ring fusion to ring B, the relative stereochemistry of the C-7 groups on the cyclobutane ring, the AC ring fusion and the configuration of the C-11 secondary Me group.

The *E*-configuration of the 2(4)-double bond was determined by NOE measurements on the triol (**1**). Irradiation of the C-1 hydroxymethylene protons gave a 17% increase in the integral for the 4-H. Significant NOE's were also observed between the 18-H_2 and H-16 (17%), H-17 and H-16 (12%) and H_2-18 (17%), H-16 and H-18 (15%) idicative of a *cis*-arrangement of these groups on the cyclobutane ring.

This is supported by the following observations: The formation of the *cis*-ethylidene derivative (**18**) after epimerisation at C-16 requires the 16-H in **1** to be *cis* to the C-18 OH group. Since the keto acid (**21**) is stable to exchange conditions with DCl–AcOD the BC ring fusion in compound **21** must be the more stable *cis*. The possibility of prior inversion during Jones oxidation of **20** can be excluded since borohydride reduction of **21** gives the parent hydroxy acid along with the C-16 epimer (**35**) which lactonizes readily. Thus **20**, and therefore **1**, must contain a *cis*-BC ring fusion. The inversion at C-16 in **15** can be rationalized if the acetyl group is in fact *cis*-to ring C and its substituents (C-12 and C-9). The relative stereochemistry at C-12 is indicated from the fact that the hydroxy acid (**20**) could not be lactonized whereas the epimer **35** readily formed a lactone (**36**).

From an examination of Dreiding models it is clear that a stable lactone is more likely to result from a *cis* disposition of the C-16 hydroxyl and the C-12 carboxymethyl substituents.

Furthermore the 12-H in lactone (**30**) appears as a brd, J 5Hz, suggesting a small dihedral angle between the 12 and 17-H, whereas in the alternative AC-*trans* fused arrangement the dihedral angle is restricted to 180° as demonstrated by the 12β-H resonances in the epimeric lactone **26** and the derived hydroxy acid **27** in which the signal appears a broadened triplet ($J_{AX} + J_{BX} \sim$ 18Hz) consistent with contiguous axial protons at C-11, C-12 and C-17. With all the ring fusions assigned as *cis* the configuration of the C-11 secondary Me group follows from the deshielding influence associated with the introduction of a CO at C-13. A comparison of the NMR spectra of **12**, **23**, **24** and **25** shows that the CO at C-13 deshields the C-20 protons by 23Hz (**12** → **23**; **12** → **24** 15Hz deshielding). In the C-12 epimer (**25**) the resonance of this Me group showed elimination of the deshielding influence.

Furthermore, in the NMR spectrum of **23**, containing $Eu(dpm)_3$ shift reagent the 12-H appears as a sharp doublet (J 9Hz) with coupling to the 17-H. Thus there is little or no coupling to the 11-H suggesting that the dihedral angle between 11-H and 12-H is close to 90° and supporting the assignment of a β-Me at C-11.

These conclusions regarding the relative configuration of the decipiene diterpenes have been confirmed[10] by X-ray crystallographic analysis of the hydroxy acid (**2**) and evidence for their absolute configuration as shown in **1**, **2** and **3** is presented in the accompanying paper.[11]

EXPERIMENTAL

General experimental details have been described.[12]

Extraction of Eremophila decipiens. The leaves and terminal branches (20 kg) of *E. decipiens*, collected between Dumbleyung and Kulin in Western Australia, were soaked in acetone for 10 min. The extract (1.5 kg) obtained was dissolved in ether and fractionated into neutral (200 g), Na_2CO_3 soluble (800 g) and NaOH soluble (300 g) fractions. Extensive separation of the neutral fraction by column chromatography (Alumina, Act IV) yielded 1,18,19-trihydroxy-decipi-2(4),14-diene (**1**) (5 g) which crystallized from acetone/n-pentane as needles, m.p. 117–120°, $[\alpha]_D$ −43° (*c*, 1.0) (Found: C, 74.6; H, 10.2. $C_{20}H_{32}O_3$ requires: C, 75.0; H, 10.1%). ν_{max}^{nujol}:

[b] Exposure of the keto-acetate corresponding to **29** to mineral acid also gave an equilibrium mixture of the 12β- and 12α-epimers (4:1).

3200 cm^{-1}; NMR (C_5D_5N) δ: 0.92 (d, J 6Hz, 20-H_3), 1.79 (s, 3-H_3), 2.72 (ddd, J ≃ J' ≃ J'' ≃ 9Hz, 17-H), 3.17 (d, J 9Hz, 16-H), 3.98, 4.23 and 4.39 (s, 18-, 19-, 1-H_2), 5.77 (brt, J 7Hz, 4-H), 6.17 (m, $W_{\frac{1}{2}}$ 10Hz, 14-H). MS: *m/e* 320 (M^+, 1%), 318 (2), 302 (50), 284 (100), 253 (50), 241 (30).

Separation of the acids by column chromatography using silicic acid gave (a) 18-*hydroxydecipi*-2(4),14-*dien*-1-*oic acid* (**2**) (2 g) which crystallized from actone as plates, m.p. 167–170°, $[\alpha]_D$ −88° (*c*, 0.3) (Found: C, 75.8; H, 9.8. $C_{20}H_{30}O_3$ requires: C, 75.4; H, 9.5%). ν_{max}^{nujol}: 3300 (OH), 2500 and 1670 cm^{-1} (−CO_2H); NMR (C_5D_5N) δ: 0.95 (brd, $W_{\frac{1}{2}}$ 9 Hz, 20-H_3), 1.75 and 1.99 (s, 3-H_3 and 19-H_3), 3.91 (s, 18-H_2), 5.67 (m, $W_{\frac{1}{2}}$ 9Hz, 4-H); 7.13 (t, J 7Hz, 14-H), 10.3 (2H, -O-H). MS: *m/e* 318 (M^+, 5%), 300 (20), 227 (5), 226 (5), 201 (20), 145 (60), 132 (100); and (b) 18,19-*dihydroxydecipi*-2(4),14-*dien*-1-*oic acid* (**3**) (4 g) which crystallized from acetone as needles, m.p. 146–7°, $[\alpha]_D$ −81° (*c*, 0.6) (Found: C, 71.7; H, 9.2. $C_{20}H_{30}O_4$ requires: C, 71.8; H, 9.0%). ν_{max}^{nujol}: 3530 and 3200 cm^{-1} (-OH), 1650 (CO_2H); NMR (C_5D_5N) δ: 0.92 (d, J 6Hz, 20-H_3), 1.90 (s, 3-H_3), 3.82 and 4.18 (s, 18-, 19-H_2), 6.00 (m, $W_{\frac{1}{2}}$ 10Hz, 14-H), 6.95 (brt, 4-H). MS: *m/e* 334 (M^+, 5%), 316 (20), 298 (40), 217 (40), 199 (50), 197 (20), 135 (70), 119 (100).

Interrelation of **3** and **1**. The diol acid **3** (500 mg) was methylated with CH_2N_2 and the ester obtained was reduced with LAH/$AlCl_3$ (200 mg, mole:mole) in ether to give **1** (250 mg) as needles, m.p. 117–120° alone or on admixture with the naturally occurring compound.

Interrelation of **1** *and* **2**. (a) **1** (1.5 g) was acetylated with Ac_2O/pyridine and the triacetate obtained (1.6 g) in EtOH was hydrogenated over Pd/C (200 g) to yield **4** (1.1 g) as an oil, b.p. (bath) 180°/0.1 mm, $[\alpha]_D$ −42° (*c*, 0.7) (Found: C, 79.6; H, 10.9. $C_{22}H_{36}O_2$ requires: C, 79.5; H, 10.9%). $\nu_{max}^{CS_2}$: 1730 cm^{-1}; NMR δ 0.8 to 1.0 (9H, 1-, 3- and 20-H_3), 1.65 (s, 19-H_3), 2.09 (s, acetate), 4.19 (s, 18-H_2), 5.62 (m, $W_{\frac{1}{2}}$ 9Hz, 14-H). MS: *m/e* 332 (M^+, 5%), 272 (20), 257 (10), 187 (10), 145 (20), 132 (100), 119 (50). (b) The hydroxy acid **2** (500 mg) was methylated with CH_2N_2 and the resulting ester was reduced with LAH/$AlCl_3$ as described above. The diol (**9**) obtained was acetylated in the usual way and the diacetate was hydrogenated over Pd/C (30 mg) to give **4** (200 mg) identical in all respects with the sample prepared in (a).

Preparation of decipiane (**8**). A soln of **4** (100 mg) in EtOH was hydrolysed with KOHaq to yield **5** as a crystalline solid, m.p. 48–52°, which could not be recrystallized, $[\alpha]_D$ −21° (*c* 3.5) (Found: M^+ 290.2627. $C_{20}H_{34}O$ requires: M^+ 290.2610). NMR ($CDCl_3$) δ: 5.59 (m, 14-H), 3.68 (AB part of an ABX system, 1-H_2), 1.66 (brs, 19-H_3), 0.91 (d, J 6Hz, 1-, 3-, 20-H_3); ν_{max} 3500 cm^{-1}. MS: *m/e* 290 (M^+, 11%), 272 (7), 159 (13), 145 (23), 132 (84), 119 (100). The alcohol (**5**) (1.9 g) in acetone (20 ml) was treated with one equivalent of Jones reagent (1.66 ml) at 0° for 20 min to give **6** (1.6 g) as an oil. A soln of **6** (1.3 g) KOH (500 mg) and hydrazine hydrate (0.5 ml) in diethylene glycol (2 ml) was heated at 130° under N_2 for 1 hr. The temperature was then raised to 195–200° and maintained for 2 hr. The reaction mixture was then cooled, poured into 2M HCl and extracted with ether. Removal of the solvent followed by preparative tlc gave **7** (100 mg) as an oil b.p. (bath) 135°/1.0 mm, $[\alpha]_D$ −46° (*c*, 1.7) (Found: C, 87.2; H, 12.4. $C_{20}H_{34}$ requires: C, 87.5; H, 12.5%). NMR (CCl_4) δ: 0.8 to 1.0 (9H, 1-, 3-, 20-H_3), 1.25 (s, 18-H_3), 1.63 (s, 19-H_3), 5.5 (m, $W_{\frac{1}{2}}$ 9Hz, 14-H). MS: *m/e* 274 (M^+, 15%), 189 (5), 119 (100). A soln of **7** (100 mg) in AcOH (30 ml) containing PtO_2 (20 mg) was stirred under a H_2 atmosphere for 24 hr. Recovery of the product gave *decipiane* **8** (80 mg) as an oil. (Found: C, 87.0; H, 13.4; M^+, 276.2810. $C_{20}H_{36}$ requires: C, 86.9; H, 13.1%; M^+, 276.2817). NMR (CCl_4) δ: 0.86 (12H, br.d, J 6Hz, 1-, 3-, 19- and 20-H_3), 1.25 (s, 18-H_3). MS: *m/e* 276 (M^+, 50%), 191 (5), 160 (10), 135 (10), 122 (100).

Isolation of the hydroxy ether **10**. The neutral fraction (380 g) from an extract of *E. decipiens* was acetylated with Ac_2O/pyridine. A soln of this "crude acetate" fraction (400 g) in ether (1.5 l) containing t-BuOH (400 ml) was added, over 4 hr, to a stirred solution of liq NH_3 (2.5 l) containing Li (50 g). The reaction was terminated by the careful addition of NH_4Cl (40 g) and the NH_3 was allowed to evaporate. The organic material (250 g) recovered with ether was dissolved in EtOH and hydrogenated over 10% Pd/C (10 g). The product obtained was adsorbed on a column of Alumina (Act I, 5 kg). Elution with light petroleum gave **7** (15 g) identical with the sample prepared as described above. Elution with light petroleum/$CHCl_3$ (4:1) gave **5** (50 g) identified by comparison with a sample prepared above. Further elution with light petroleum/$CHCl_3$ (1:1 to 1:5) gave fractions (70 g) containing a new compound. Purification of a small portion of this material gave **10** as an oil. (Found: M^+ 304.24001. $C_{20}H_{32}O_2$ requires: M^+ 304.24023). $\nu_{max}^{CS_2}$: 3500 cm^{-1}; NMR (CCl_4) δ: 0.8 to 1.0 (6H, 3-, 20-H_3), 1.62 (s, 19-H_3), 3.05 (m, $W_{\frac{1}{2}}$ 10Hz, 4-H), 3.48 (d, J 6Hz, 1-H_2), 3.31 and 3.85 (AB part of an ABX system, J_{AB} 11.5Hz, J_{BX} 2Hz, 18-H_2), 5.5 (m, $W_{\frac{1}{2}}$ 9Hz, 14-H). MS: *m/e* 304 (M^+, 5%), 245 (20), 227 (10), 145 (30), 132 (40), 119 (100).

4,18-*Epoxydecipi*-14-*ene* (**12**). The ether **10** (65 g) was treated with *p*-toluenesulphonyl chloride (50 g) in pyridine (500 ml). The tosylate **11** (57 g) obtained was dissolved in Et_2O (800 ml) and treated with LAH (20 g) for 6 hr. Recovery of the product with ether yielded **12** (25 g) as an oil, b.p. (bath) 130°/0.1 mm, $[\alpha]_D$ −60° (*c*, 2.2) (Found: C, 83.1; H, 11.0. $C_{20}H_{32}O_2$ requires: C, 83.3; H, 11.2%). NMR (CCl_4) δ: 0.7 to 1.0 (9H, 1-, 3-, 20-H_3), 1.58 (s, 19-H_3), 2.82 (m, partly obscured, 4-H), 3.25 and 3.81 (AB part of an ABX system, J_{AB} 11.5 Hz, J_{BX} 2 Hz, 18-H_2), 5.5 (m, $W_{\frac{1}{2}}$ 9 Hz, 14-H). Addition of Eu(dpm)$_3$ gave the following shifts (in Hz/mg of shift reagent) 4-H (2.75), 18-H_2 (2.3 and 2.6), 1-, 3-H_3 (0.8 and 1.2). MS: *m/e* 288 (M^+, 40%), 270 (5), 245 (100), 227 (20), 202 (30).

Correlation of the hydroxy ether (**10**) *with the triol* (**1**). A soln of **11** (7.5 g) and t-KOBu (18 g) in DMSO (300 ml) was stirred under N_2 for 2 hr at room temp. The mixture was diluted with Et_2O (2.0 l) and washed repeatedly with H_2O. Removal of the solvent followed by silicic acid chromatography yielded **13** (1.5 g) as an oil, b.p. (bath) 170°/1.0 mm, $[\alpha]_D$ −75° (*c*, 1.2) (Found: C, 83.8; H, 10.5. $C_{20}H_{30}O$ requires: C, 83.9; H, 10.6%). NMR ($CDCl_3$) δ: 0.93 (d, J 6Hz, 20-H_3), 1.64 and 1.72 (s, 3-, 19-H_3), 3.66 (dd, J 4Hz, J 8Hz, 4-H), 3.46 and 3.98 (AB part of an ABX system, J_{AB} 11Hz, J_{BX} 2Hz, 18-H_2), 4.81 and 4.95 (brs, $W_{\frac{1}{2}}$ 5Hz, 1-H_2), 5.6 (m, $W_{\frac{1}{2}}$ 9Hz, 14-H). MS: *m/e* 286 (M^+, 30%), 271 (5), 268 (4), 202 (20), 119 (100), 93 (60). A soln of **13** (200 mg) in ether (30 ml) and ethylamine (30 ml) was treated with Li metal (0.5 g).

After 15 min EtOH (1 ml) was added and the product (180 mg) isolated with ether, was hydrogenated over 10% Pd/C. The hydrogenated compound after acetylation afforded **4** (100 mg) identical with a sample prepared from **1** as described above.

4-*Hydroxydecipian*-18-*oic acid* 4,18-*lactone* (**14**). A soln of **13** (150 mg) in AcOH (10 ml) was hydrogenated over PtO_2 for 24 hr to yield the dihydro compound (120 mg) as an oil (M^+, 290). A sample of this compound (100 mg) in CCl_4 (10 ml) was treated with excess RuO_4 (10 mg) in CCl_4 for 1 hr. Isopropanol (1 ml) was then added and the reaction mixture was filtered through celite. Evaporation of the solvent gave **14** (40 mg) which crystallised from acetone/n-pentane as needles, m.p. 94–8°, $[\alpha]_D$ −48° (*c*, 0.1) (Found: M^+, 304.23767. $C_{20}H_{32}O_2$ requires: M^+, 304.24023). $\nu_{max}^{CS_2}$: 1720 cm^{-1}; NMR (CCl_4) δ: 0.7 to 1.0 (12H, 1-, 3-, 19-, 20-H_3), 2.98 (q, J 9Hz, 17-H), 3.82 (m, $W_{\frac{1}{2}}$ 20Hz, 4-H). MS: *m/e* 304 (M^+, 20%), 286 (15), 261 (15), 162 (100), 121 (30), 119 (50).

Ozonolysis of **4**. Oxygen containing O_3 was passed through a soln of **4** (20 g) in $CHCl_3$ (100 ml) and pyridine (2 ml) at −70° until excess ozone could be detected. The solvent was removed under reduced pressure and the residue (20 g) in acetone (80 ml) was treated with excess Jones reagent for 20 min at room temp. The product (18 g) recovered was then separated into acidic (8 g) and neutral (9.5 g) components. Chromatography of the methylated acidic components gave **15** (3.0 g) which crystallised from pentane as needles, m.p. 57–61°; $[\alpha]_D$ +36° (*c*, 2.3) (Found: C, 69.9; H, 9.6 $C_{23}H_{38}O_5$ requires: C, 70.0; H, 9.7%). ν_{max}: 1710, 1745 cm^{-1}; NMR ($CHCl_3$) δ: 0.8 to 1.1 (9H, 1-, 3-, 20-H_3), 1.96 and 2.13 (s, acetoxymethyls), 3.65 (s, −CO_2CH_3), 4.05 (s, 18-H_2). MS: *m/e*

394 (M^+, 1%), 334 (20; Acc. mass 334.2507; Calc. for $C_{21}H_{34}O_3$: 334.2508), 321 (45; Acc. mass 321.2421; Calc. for $C_{20}H_{33}O_3$ 321.2430, M^+, $-CH_2CO_2Me$), 320 (30), 291 (100), 249 (70), 231 (30), 217 (100), 167 (65).

A soln of **15** (3.0 g) in $CHCl_3$ (100 ml) was treated with *m*-chloroper-benzoic acid (1 g) and *p*-TsOH (20 mg) and heated under reflux for 48 hr. The product recovered was purified by chromatography (Al_2O_3) to yield a diacetate (1.5 g) [NMR ($CHCl_3$) δ: 0.8 to 1.1 (9H, secondary methyls), 1.98 and 2.03 (s, acetoxy Me's), 3.67 (s, $-CO_2Me$), 4.22 (s, 18-H_2), 5.02 (d, J 9Hz, 16-H)] which was saponified with 10% NaOH in aq EtOH at 80° for 1 hr. The product obtained was methylated with CH_2N_2 to give, after recrystallization from ether, needles of **17** (1 g), m.p. 110–112, $[\alpha]_D$ + 53° (*c*, 0.5) (Found: C, 69.7: H, 10.4. $C_{19}H_{34}O_4$ requires: C, 69.9, H, 10.5%). $\nu_{max}^{CS_2}$: 3530, 3430 (OH), 1715 cm^{-1} (ester). NMR ($CHCl_3$) δ: 0.8 to 1.1 (9H, 1-, 3-, 20-H_3), 3.27 (s, 18-H_2), 3.70 (s, CO_2CH_3), 4.02 (d, J 9Hz, 16-H). MS: *m/e* 326 (M^+, 1%), 308 (10), 290 (10), 235 (25), 223 (100). Al_2O_3 chromatography of the neutral components obtained from the ozonolysis reaction yielded a small amount (300 mg) of the stable ozonide as an oil. NMR ($CDCl_3$) δ: 0.90 (9H, d, J 6Hz, 1-, 3-, 20-H_3), 1.40 (s, $CH_3-\overset{O}{\overset{\|}{C}}-O$), 2.00 (s, acetoxy methyl), 4.00 (s, 18-H_2), 5.62 (m, $W_{\frac{1}{2}}$ 5Hz, $H-C<^{O}_{O}$). The ozonide was stirred with Zn (1 g) in AcOH (30 ml) for 6 hr. The organic product (280 mg) recovered with ether was oxidized with excess Jones reagent for 10 min. and the resulting acid was methylated to give **16** (150 mg) as an oil. NMR ($CHCl_3$) δ: 0.7 to 1.1 (9H, 1-, 3-, 20-H_3), 2.08 and 2.17 (s, acetoxy Me's), 3.65 (s, $-CO_2CH_3$), 4.13 (s, 18-H_2). When treated with 2M HCl-AcOH in dioxan **16** afforded a compound identical to **15**. Oxidation of **15** (130 mg) with *m*-chloroperbenzoic acid in $CHCl_3$ with a trace of *p*-TsOH followed by saponification of the product and remethylation gave **17** (40 mg) m.p. 110–112°, alone or in admixture with the sample prepared above.

Ethylidene derivative of **17**. A soln of **17** (50 mg) in Et_2O (30 ml), paraldehyde (0.2 ml) and conc HCl (1 drop) was heated under reflux for 4 hr. The excess paraldehyde was removed by repeated washing of the ether soln with H_2O. Removal of the solvent gave **18** (50 mg) as an oil. (Found: $M^+ - CH_3CHO$, 308.23448. $C_{19}H_{32}O_3$ requires: M^+, 308.23440). NMR ($CHCl_3$) δ: 0.88 (6H, J 6Hz, 1-, 3-H_3), 1.02 (d, J 6Hz, 20-H_3), 1.21 (d, J 5Hz, ethylidene Me), 3.67 (s, $-CO_2CH_3$), 3.80 and 4.10 (ABq, J 12Hz, 18-H_2), 4.02 (d, J 10.5Hz, 16-H), 4.95 (q, J 5Hz, dioxymethine). MS: *m/e* 353 (M^+ + 1, 1%), 308 (30), 267 (10), 223 (30), 184 (100; Acc. mass 184.14619; Calc. for $C_{11}H_{20}O_2$, 184.14633).

Ozonolysis of **7**. The hydrocarbon **7** (10 g) was ozonised under conditions similar to those used for **4**. The product (9.4 g) recovered after oxidative work-up was purified by silicic acid chromatography to give a fraction which was crystallized from n-pentane as the monohydrate form of **19** (2.5 g), needles, m.p. 55–56°, $[\alpha]_D$ + 92° (*c*, 0.4). (Found: C, 70.7; H, 10.6. $C_{20}H_{34}O_3$ requires: C, 70.5; H, 10.6%). Heating the sample to 50° under vacuum gave **19** as an oil. (Found: C, 74.3; H, 10.8. $C_{20}H_{34}O_3$ requires: C, 74.5; H, 10.6%). $\nu_{max}^{CS_2}$: 2700–3300 (OH), 1710 cm^{-1} (carbonyl). NMR ($CHCl_3$) δ: 0.8 to 1.1 (9H, 1-, 3-, 20-H_3), 0.95 (s, 18-H_3), 2.02 (s, 19-H_3). MS: *m/e* 322 (M^+, 10%), 307 (8), 302 (10), 264 (40), 262 (40), 237 (100), 219 (40).

Bayer–Villiger oxidation of the methyl ester of **19**. The keto acid **19** (2 g) was methylated with MeI/K_2CO_3 in acetone. The ester (2 g) in CH_2Cl_2 (100 ml) was treated with *m*-chloroperbenzoic acid (2 g) and *p*-TsOH (10 mg) and the mixture left for 24 hr at room temp. The product obtained was saponified with 10% NaOH in aq EtOH at 80° for 1 hr. The mixture was acidified with 2NHCl and the product recovered with ether gave **20** (1.2 g) which crystallised from $CHCl_3$ as needles, m.p. 162–4°, $[\alpha]_D$ + 46° (*c*, 0.5) (Found: C, 73.1: H, 10.7. $C_{18}H_{32}O_3$ requires: C, 72.9; H, 10.9%. ν_{max}^{nujol}: 3320 (OH), 1690 cm^{-1} (carbonyl). NMR (C_5D_5N) δ: 0.88 (6H, d, J 6Hz, secondary methyls), 1.07 (d, J 6Hz, secondary Me), 1.20 (s, 18-H_3), 4.08 (d, J 9Hz, 16-H). MS: *m/e* 296 (M^+, 5%), 278 (20), 218 (25), 193 (25), 179 (30), 142 (100).

Oxidation of the hydroxy acid (**20**). A soln of **20** (1 g) in acetone (30 ml) was oxidized with excess Jones reagent at 0° and yielded **21** (900 mg) which crystallised fron n-pentane as needles, m.p. 86–90°, $[\alpha]_D$ + 46° (*c*, 0.1) (Found: C, 73.5: H, 10.2. $C_{18}H_{30}O_3$ requires: C, 73.4; H, 10.3%). $\nu_{max}^{CCl_4}$: 1762 (ketone), 1700 cm^{-1} (acid). NMR (C_5D_5N) δ: 0.97 (6H, J 6Hz, 1-, 3-H_3), 1.04 (d, J 6Hz, 20-H_3), AMNX pattern at δ_A 2.44 (12-H), δ_M 2.83 (13-H), δ_N 3.11 (13-H), δ_X 3.81 (17-H), J_{AX} 9Hz, J_{AM} 6.5 Hz, J_{AN} 8 Hz, J_{MN} 15 Hz). MS: *m/e* 294 (M^+, 5%), 292 (10), 276 (7), 209 (10), 206 (15), 153 (20), 140 (100). Treatment of **21** (25 mg) with 2MDCl-AcOD for 24 hr at room temperature yielded a monodeuterated derivative as a crystalline solid (20 mg). NMR (C_5D_5N) as for **20** except that the dd at 3.81 was not present and the 12-H at δ 2.44 had lost a 9 Hz coupling'. Treating **20** under the same conditions using 2M HCl-AcOH in dioxan afforded only the starting material, m.p. 84–88°, undepressed on admixture.

Allylic oxidation of **4**. A slurry of $CrO_3.Py_2$ complex (70 g) in CH_2Cl_2 (200 ml) was added to a stirred soln of **4** (25 g) in CH_2Cl_2 (1.0 l) under N_2. Similar quantities of the complex in CH_2Cl_2 were added after 6, 12 and 20 hr and the soln was left for a further 20 hr. The mixture was decanted from the tarry ppt which was washed with ether. The combined organic layer was washed with 5% NaOH, 2M HCl and brine and dried over Na_2SO_4. Removal of the solvent gave an oily residue which was separated by alumina chromatography into fractions of starting material (12 g) and **22** (10 g) as an oil, $[\alpha]_D$ − 111° (*c*, 2.2) (Found: M^+, 346.24992. $C_{22}H_{34}O_3$ requires: M^+, 346.25079). ν_{max}^{film}: 1745 (ester), 1665 (conjugated ketone). NMR ($CDCl_3$) δ: 0.84 (6H, d, J 6Hz, 1-, 3-H_3), 1.34 (m, $W_{\frac{1}{2}}$ 6 Hz, 20-H_3), 1.83 (d, J 1 Hz, 19-H_3), 2.09 (s, acetoxy Me), 2.74 (d, J 9Hz, 16-H), 3.07 (ddd, J = J' = J'' = 9Hz, 17-H), 4.15 and 4.23 (ABq, J_{AB} 11Hz, 18-H_2), 5.88 (q, J 1Hz, 14-H). Addition of Eu(dpm)$_3$ allowed the 12-H to be clearly seen as a doublet (J 9Hz). MS: *m/e* 346 (M^+, 5%), 303 (5), 286 (20), 161 (40), 135 (100), 108 (100).

Allylic oxidation of **12**. The ether **12** (20 g) was oxidized with $CrO_3.Py_2$ complex in a manner similar to that described for **4**. Chromatography of the oxidation mixture on alumina and elution with light petroleum gave starting material (5 g). Elution with light petroleum-$CHCl_3$ mixtures gave **23** (5.2 g) as an oil which crystallised from isopentane as needles, m.p. 70–70.5°, $[\alpha]_D$ − 213° (*c*, 2.3) (Found: C, 79.4; H, 9.9. $C_{20}H_{30}O_2$ requires: C, 79.4; H, 10.0%). ν_{max}^{nujol}: 1650 cm^{-1} (ketone); NMR (CCl_4) δ: 0.77 to 0.95 (6H, 1-, 3-H_3), 1.33 (brs, $W_{\frac{1}{2}}$ 5Hz, 20-H_3), 1.80 (d, J 1Hz, 19-H_3), 2.85 (2H, m, $W_{\frac{1}{2}}$ 30Hz, 4-H, 17-H), 3.31 and 3.89 (AB part of an ABX system, J_{AB} 11.5Hz, J_{BX} 2Hz, 18-H_2), 5.75 (q, J Hz, 14-H). MS: *m/e* 302 (M^+, 20%), 259 (10), 241 (5), 135 (100); λ_{max}^{EtOH}: 257 nm (ε 2500).

4,18-*Epoxy*-13-*oxo*-12α-*decipiane* (**24**). A soln of **23** (3.52 g) in ether (20 ml) and t-BuOH (1.0 ml) was added to Li (240 mg) in NH_3 (80 ml). After 1 min the reaction was terminated by the addition of NH_4Cl (200 mg) and worked up the usual way. The product obtained as an oil was the 12α-*epimer* **24** (3.2 g) (Found: M^+, 304.2403. $C_{20}H_{32}O_2$ requires: M^+, 304.2402), $\nu_{max}^{CS_2}$: 1705 cm^{-1} (CO); NMR (CCl_4) δ: 0.8 to 1.0 (9H, 1-, 3-, 19-H_3), 1.22 (m, $W_{\frac{1}{2}}$ 6Hz, 20-H_3), 2.90 (2H, m, 4-H and 17-H), 3.24 and 3.82 (AB part of an ABX system J_{AB} 11.5Hz, J_{BX} 2Hz, 18-H_2). MS: *m/e* 304 (M^+, 30%), 261 (10), 243 (30), 195 (35), 110 (100), Acc. mass 110.0728; Calc. for $C_7H_{10}O$, 110.0732). Attempts to purify **24** by chromatography on alumina gave the 12β-epimer (**25**) as an oil, $\nu_{max}^{CS_2}$: 1710 cm^{-1} (carbonyl): NMR (CCl_4) δ: 0.8 to 1.0 12H, secondary methyls), 2.85 (m, $W_{\frac{1}{2}}$ 18 Hz 4-H), 3.23 and 3.67 (AB part of an ABX system, J_{AB} 11.5Hz, J_{BX} 2Hz, 18-H_2). MS: *m/e* 304 (M^+, 100%), 361 (100), 243 (30), 166 (100). The compound was characterized as the semicarbazone derivative which crystallized from acetone as needles, m.p. 215–220°. (Found: C, 70.0; H, 9.9; N, 11.3. $C_{21}H_{35}O_2N_3$ requires: C, 70.0; H, 9.8; N, 11.6%). Treatment

of either **24** or **25** with 2M HCl/AcOH in dioxan for 24 hr yielded the same equilibrium mixture containing **24** and **25** in 1:4 ratio as estimated from the intensity of the ether methylene signal in the NMR spectrum and from tlc analysis.

Bayer–Villiger oxidation of **25**. A soln of **25** (200 mg) in CH_2Cl_2 (30 ml) containing *m*-chloroperbenzoic acid (400 mg) and *p*-TsOH (10 mg) was left at room temperature for 48 hr. The product recovered was purified by preparative tlc to give **26** (100 mg) as an oil. NMR (CCl_4) δ: 0.8–1.1 (12H, secondary Me's), 3.23 and 3.57 (AB part of an ABX system, J_{AB} 11.5Hz, J_{BX} 2Hz, 18-H_2), 4.45 (brt, J 9Hz, 12-H). The same lactone was obtained on similar treatment of **24**. On standing **26** absorbed a mole of water to give **27** (100 mg) which crystallised from acetone as plates, m.p. 166–8°, $[\alpha]_D$ −42° (*c*, 0.6) (Found: C, 70.9; H, 10.3. $C_{20}H_{34}O_4$ requires: C, 70.9; H, 10.1%). ν_{max}^{nujol}: 3320 (OH), 1700 cm^{-1} (CO); NMR (C_5H_5N) δ: 0.8 to 1.2 (12H, secondary Me's), 2.90 (m, $W_{\frac{1}{2}}$ 18Hz, 4-H), 3.42 and 3.66 (AB part of an ABX system, J_{AB} 11.5Hz, J_{BX} 2Hz, 18-H_2), 3.90 (m, $W_{\frac{1}{2}}$ 20Hz, 12-H). MS: *m/e* 320 (M^+, 20%), 277 (60), 259 (100).

Oxidation of the hydroxy acid (**27**). A soln of **27** (50 mg) in acetone (5 ml) was treated with excess Jones reagent for 10 min at 0°. The product recovered crystallised from acetone-n-pentane as prisms of **28** (30 mg), m.p. 170–2°. (Found: $M^+ - C_3H_7$, 293.17528. $C_{17}H_{25}O_4$ requires: 293.17541). $\nu_{max}^{CS_2}$: 1700 cm^{-1} (carbonyl). MS: *m/e* 337 ($M^+ + H$, 1%), 336 (M^+, 1), 293 (10), 275 (15), 257 (10), 249 (15), 226 (90, Acc. mass 226.15677, Calc. for $C_{13}H_{22}O_3$, 226.15689), 111 (100), Treatment of **28** with 2M DCl/AcOD in dioxan for 24 hr yielded the dideutero derivative which showed MS peaks at *m/e* 338 (M^+, 1), 226 (90), 113 (100).

18-*Benzoyloxy*-13-*oxo-decipiane* (**29**). A soln of **23** (8 g), ether (40 ml) and t-BuOH (5 ml) was added to a stirred solution of Li (600 mg) in NH_3 (100 ml). The excess Li was destroyed by the addition of NH_4Cl and the organic product (7 g) recovered with ether. Treatment of the crude alcohol with benzoyl chloride in C_5H_5N gave **29** (6 g) as an oil, b.p. 260° (bath)/0.1 mm. (Found: C, 79.0; H, 9.2. $C_{27}H_{38}O_3$ requires: C, 79.0; H, 9.3%). $\nu_{max}^{CS_2}$: 1705 cm^{-1}; NMR (CCl_4) δ 0.7 to 1.1 (9H, secondary Me's), 1.20 (m, $W_{\frac{1}{2}}$ 6Hz, 20-H_3), 4.35 (s, 18-H_2), 7.2–8.2 (5 aromatic protons). MS: *m/e* 410 (M^+, 5%), 392 (2), 288 (20), 179 (70), 110 (100), 105 (100).

Bayer–Villiger oxidation of **29**. A soln of **29** (5.5 g) in $CHCl_3$, *m*-chloroperbenzoic (3 g) and *p*-TsOH (20 mg) was left for 48 hr at room temp. Recovery of the product gave **30** (4.5 g) as an oil. $\nu_{max}^{CS_2}$: 3600, 3500 (OH), 1720 cm^{-1} (CO). NMR ($CDCl_3$) δ: 0.7 to 1.1 (12H, secondary Me's), 4.34 (s, 18-H_2), 4.38 (m, $W_{\frac{1}{2}}$ 5Hz, 12-H), 7.3 to 8.2 (5 aromatic protons). MS: *m/e* 426 (M^+, 1%), 321 (2), 304 (30), 217 (30), 105 (100). The lactone **30** (2 g) was saponified with 10% NaOH in aq. EtOH at 80° for 1 hr. The acid recovered was methylated with CH_2N_2 and the product was purified by alumina chromatography to give fractions which crystallised from acetone–n–pentane as prisms of **31** (0.5 g), m.p. 107–108°, $[\alpha]_D$ + 10 (*c*, 1.1) (Found: C, 71.2; H, 10.9 ($C_{11}H_{38}O_4$ requires: C, 71.1; H, 10.8%). $\nu_{max}^{CS_2}$: 3600, 3500 (OH), 1720 cm^{-1} (ester). NMR ($CDCl_3$) δ: 0.8 to 1.0 (12H, secondary Me's), 3.52 (s, 18-H_2), 3.67 (s, CO_2Me), 3.95 (m, $W_{\frac{1}{2}}$ 6Hz, 12-H). MS: *m/e* 354 (M^+, 5%), 337 (9), 336 (8), 319 (50), 235 (20), 221 (25), 217 (15), 168 (100), 95 (100).

Methyl 18-*benzoyloxy*-12-*oxo*-12,13-*secodecipian*-13-*oate* (**32**). A soln of the **31** (400 mg) in C_5H_5N (10 ml) containing benzoyl chloride (1.2 mole equiv) was left for 6 hr at 0° to give the monobenzoate ester (300 mg) as an oil. NMR ($CDCl_3$) δ: 0.8 to 1.05 (12H, secondary Me's), 3.66 (s, CO_2Me), 3.95 (m, $W_{\frac{1}{2}}$ 7Hz, 12-H), 4.19 and 4.33 (ABq, J 11Hz, 18-H_2), 7.2 to 8.2 (5 aromatic protons). Oxidation of the monobenzoate ester (280 mg) with Jones reagent gave the **32** (250 mg) as an oil. (Found: M^+, 456.28595. $C_{28}H_{40}O_5$ requires: M^+, 456.28745). $\nu_{max}^{CS_2}$: 1735, 1720 and 1700 cm^{-1} (CO's). NMR ($CDCl_3$) δ: 0.8 to 1.0 (9H, secondary Me's), 3.36 (s, $-CO_2Me$), 4.14 and 4.30 (ABq, J 11Hz, 18-H_2), 7.2 to 8.2 (5 aromatic protons). MS: *m/e* 456 (M^+, 1%), 334 (10), 304 (10), 303 (10), 302 (10), 261 (10), 233 (20), 224 (20), 217 (20), 105 (100).

Methyl-18-*benzyloxy*-12-*oxo*-12,13-*secodecipi*-10-*en*-13-*oate* (**34**). A soln of **32** (174 mg) and trimethylphenyl ammonium bromide perbromide (142 mg) in THF (10 ml) was stirred at 0° for 30 min. After addition of dil $Na_2S_2O_3/NaHCO_3$ (0.1 ml) the mixture was extracted with ether to give **33** (140 mg) as an oil. NMR ($CDCl_3$) δ: 0.8 to 1.0 (9H, secondary Me's), 1.85 (s, 20-H_3), 3.67 (s, CO_2Me), 4.13 and 4.29 (ABq, J 11Hz, 18-H_2), 7.2 to 8.2 (5 aromatic protons). A soln of **33** (100 mg), anhy LiCl (100 mg) in DMF (10 ml) was heated to 50° for 1 hr. The soln was cooled, diluted with water and extracted with Et_2O to give **34** (40 mg) as an oil. (Found: $M^+ - C_6H_5CO_2H$, 332.23103. $C_{21}H_{32}O_3$ requires: 332.23514). $\nu_{max}^{CS_2}$: 1735, 1720 and 1685 cm^{-1} (CO's); λ_{max}^{EtOH}: 244 nm. NMR ($CDCl_3$) δ: 0.8 to 1.0 (9H, secondary Me's), 1.82 (d, J 2Hz, 20-H_3), 3.67 (s, CO_2Me), 4.37 and 4.19 (ABq, J 11.5Hz, 18-H_2), 6.64 (brt, J 4Hz, 10-H). MS: *m/e* 454 (M^+, 5%), 423 (5), 333 (30), 332 (25), 231 (40), 224 (30), 105 (100).

$NaBH_4$ *Reduction of the keto acid* (**21**). A soln of **21** (200 mg) in MeOH (50 ml) was treated with $NaBH_4$ (500 mg) for 72 hr. The product (185 mg) recovered was separated by preparative tlc to give **21** (20 mg), **20** (30 mg) which crystallised from $CHCl_3$ as needles, m.p. 162–4° alone or in admixture with the sample prepared previously, and **35** (80 mg) as an oil, b.p. 180° (bath)/0.8 mm. (Found: C, 77.7; H, 10.9 $C_{18}H_{30}O_2$ requires: C, 77.7 H, 10.9%). $\nu_{max}^{CS_2}$: 1745 (lactone); NMR ($CDCl_3$) δ: 0.8 to 1.0 (9H, secondary Me's), 1.20 (s, 18-H_3), 4.35 (dd, J 6, 3Hz, 16-H). MS: *m/e* 278 (M^+, 50%), 263 (5), 250 (10), 193 (50), 137 (80), 124 (100). Saponification of **35** with 10% NaOH in aq EtOH at 80° for 1 hr gave, after acidification of the mixture, an oil identical by NMR and tlc with **35**. Treatment of **20** in ether with DCC for 6 hr yielded starting material.

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