β-Stereospecific Hydroboration of 13-*epi*-Pimar-8(14)-enes

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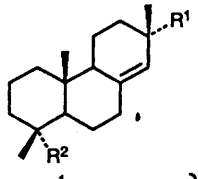
β-Stereospecific hydroborations of the $\Delta^{8(14)}$-double bond in 13-*epi*-pimarenes were achieved in the absence of functional groups at C-16 or a double bond at C-15. The reaction carried out on 15,16-dihydrosandaracopimaric derivatives needed more time and a large excess of reagent due to stereochemical restrictions in the transition state.

In a previous paper[1] we reported the results obtained on the hydroboration of the $\Delta^{8(14)}$-double bond of 16-*O*-substituted 13-*epi*-pimarenic derivatives **1a**, that was β-stereospecific only when the substituent X was the voluminous $SiPh_2Bu^t$ group. The observed results could be accounted for by an increase in β-attack as a consequence of the increase of the X substituent's volume fairly well, although this influence might not be so important due to the distance between the X group and the $\Delta^{8(14)}$-double bond. Therefore, the stereochemistry of the hydroboration of 13-*epi*-pimaradienes **1b** and derivatives **1a** must be explained by other factors.



1a $R^1 = CH_2CH_2OX$
1b $R^1 = CH{=}CH_2$
1c $R^1 = Et$
} $R^2 = CO_2Me, CH_2OAc$

The possible formation of cyclic boranes as intermediates[1] in the hydroboration–oxidation of diene **1b**[2,3] together with the progressive loss of association between the reagent and the oxygen atom at C-16 as the X substituent's volume increases in the hydroboration of silylated **1a** accounts for the change from the preferred α-attack for **1b** to the β-stereoselectivity and even β-stereospecificity for compounds **1a**.

This latter explanation implies that, under the conditions employed, the reaction could follow the opposite stereochemical course when the association between the reagent and the C-16 function disappears, and that it may occur from the more hindered β-face of the diterpenic system. In order to confirm this hypothesis we carried out the hydroboration–oxidation of 13-*epi*-pimar-8(14)-enes **1c**, in which the stereochemistry of the hydroboration would be controlled only by skeletal effects.

Results and Discussion

The substances employed in the hydroboration–oxidation experiments, methyl 15,16-dihydrosandaracopimarate **3** and 15,16-dihydrosandaracopimarol acetate **4**, were obtained, respectively, by selective hydrogenation of the Δ^{15}-double bond of methyl sandaracopimarate **1** and sandaracopimarol acetate **2**. Several experiments were carried out, changing the reagents [BH_3, 9-borabicyclo[3.3.1]nonane (BBN), thexylborane], temperature and reaction time (Table 1). The main products are those derived from the hydroboration of the $\Delta^{8(14)}$-double bond from the β-face (Scheme 1); namely, hydroxy ester **5** and its reduction diol **6** from methyl ester **3** and diol **6** from acetate **4**.

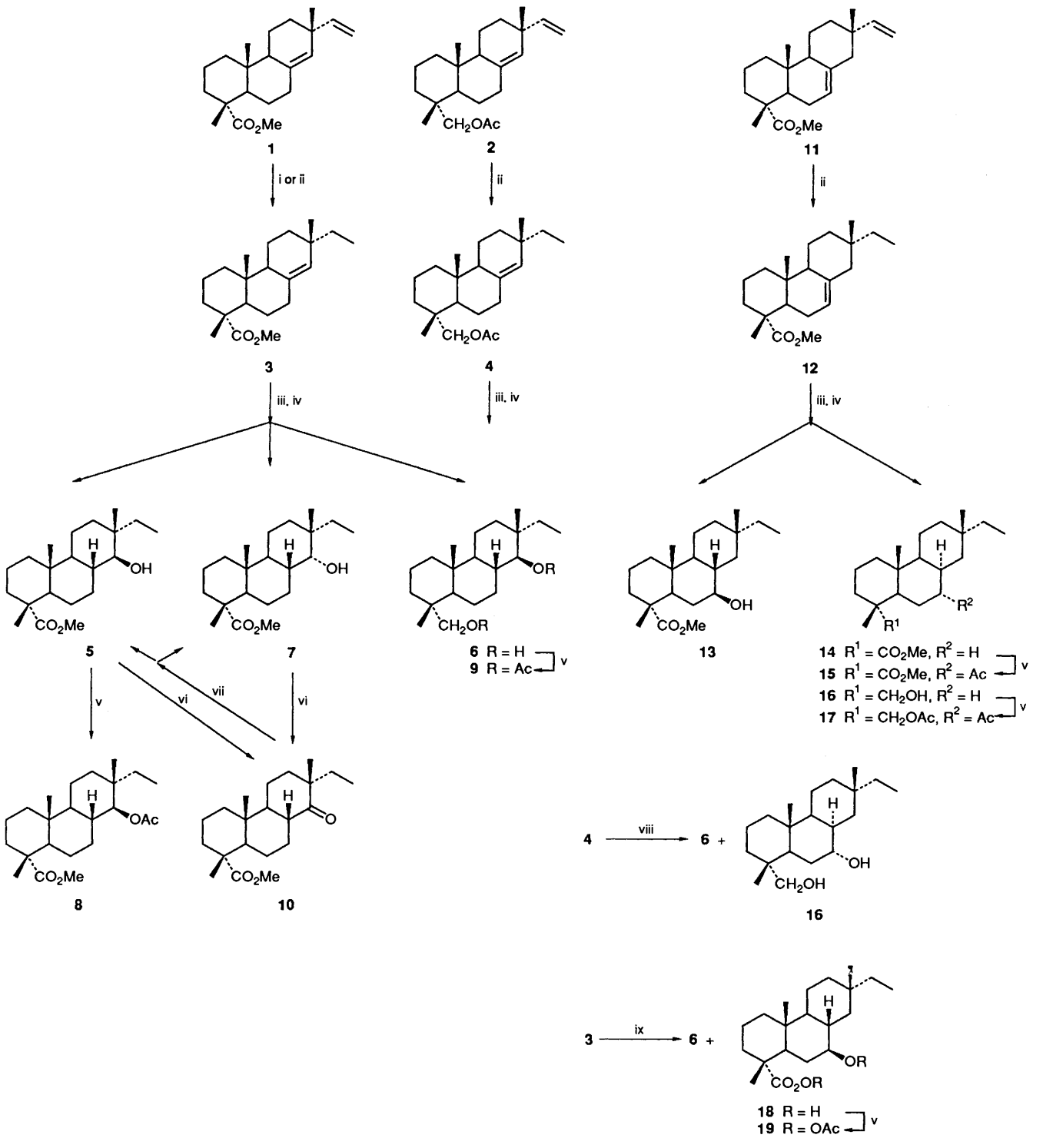
Table 1

Compound (C)	Reagent (R)	R:C	Time (*t*/h) at Temp. (*T*/°C)	Products
3	BH_3·THF	6	1 at 0 and 8 at 25	**5** (57%), **6** (10%), **7** (10%)
4	BH_3·THF	6	1 at 0 and 8 at 25	**6** (88%)
4	BH_3·THF	1.5	1 at 0 and 8 at 25	unchanged **4**
4	BH_3·THF	1.5	1 at 0 and 96 at 25	**6** (40%), **16** (15%)
12	BH_3·THF	6	1 at 0 and 3 at 25	**13** + **14** (22%), **14** (54%), **16** (4%)
4	BBN	2.5	6 at 40 and 12 at reflux	unchanged **4**
4	BBN	5.3	72 at reflux	unchanged **4**
4	Thexylborane	4.0	96 at 25	unchanged **4**
3	Thexylborane	4.5	42 at reflux	**6** (15%), **18** (7%)

The *trans*-stereochemistries of products **5** and **6** were established by comparison of their NMR data, and those of their acetates **8** and **9**, with previous assignments of other 13-*epi*-pimaranes,[4,5] the most characteristic spectral aspects being the 14-H shielding (δ 2.9) and the chemical shifts of the axial methyl group on C-13, which absorbed at δ 17.0. The *trans*-junction of the B- and C-ring was also confirmed through the oxidation of compound **5** to keto ester **10**, which remained unchanged after basic treatment in spite of the carbonyl group at C-14 that would produce epimerization of C-8 if the B–C junction were *cis*.[3,4] The products obtained in the $NaBH_4$ reduction of keto ester **10** were the alcohol **5** and its C-14 epimer **7**, both with the *trans* B–C junction.

These results were reproduced and the β-stereospecific hydroboration was observed whenever the starting material reacted. With the more hindered thexylborane or BBN reagents there was no reaction at room temperature and very low yields of hydroboration–oxidation products were achieved after reflux of the mixture for several hours.

These results demonstrate reasonably well that the hydroboration of the $\Delta^{8(14)}$-double bond in 13-*epi*-pimarene derivatives having no unsaturation or functional groups at C(15)–C(16) is β-stereospecific. This stereochemical result is unexpected if the hydroboration of other polycyclic systems,[6] the steric control of the reaction,[7] and the preferential equatorial attack of the reagent[8,9] are taken into account, since these would suggest that the (unobserved) 14α-hydroxy derivative would be obtained.



Scheme 1 *Reagents and conditions:* i, H_2, Pd/C; ii, H_2, PtO_2; iii, BH_3·THF (5 mmol), 6 h; iv, EtOH, NaOH, H_2O_2; v. Ac_2O, pyridine; vi, Jones reagent; vii, $NaBH_4$; viii, BH_3·THF (1.5 mmol), 96 h; ix, thexylborane, reflux

In order to explain the β-stereospecificity we compared the hydroboration of $\Delta^{8(14)}$- and Δ^{7}-13-*epi*-pimarenes with their epoxidation, because this latter reaction, in the absence of polar groups,[10] is mainly controlled by steric factors and gives stereochemical results comparable to those obtained in the hydroboration.[6,11] In view of the epoxidations described by ApSimon[12] and Delmond *et al.*[13,14] some facts may be considered: (i) The Δ^{7}-double bond is more accessible and reacts faster than the $\Delta^{8(14)}$-double bond. (ii) The α-face is sterically preferred in Δ^{7}-13-*epi*-pimarenes. (iii) Neither α nor β attacks are preferred in $\Delta^{8(14)}$-13-*epi*-pimarenes.

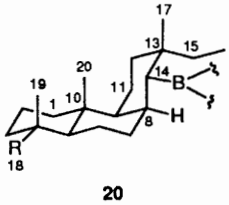
In order to confirm that the stereochemistries of both the hydroboration and the epoxidation can be compared for these substrates, we also hydroborated the methyl ester **12**. The experimental results indeed confirmed that the Δ^{7}-double bond is more accessible than the $\Delta^{8(14)}$-double bond since its hydroboration was faster at 25 °C (Table 1). Furthermore, the relative yield of the stereoisomers **13** and **14** was the same in the

hydroboration of Δ^7-13-*epi*-isopimarenes as in the epoxidation carried out by us on substrate **12**, with an approximate ratio for α- to β-attack of 6:1.

All the foregoing observations point to the β-stereospecific hydroboration of $\Delta^{8(14)}$-13-*epi*-pimarenes as a particular case that must be explained in a different way than the usual stereochemical control of hydroboration.[7]

First of all, this reaction requires more time and a large excess of reagent; this suggests the existence of very important stereochemical restrictions in the reaction. The results with BBN or thexylborane are quite consistent with this idea. Under such conditions, the intermediate boranes can evolve in several ways, changing their position and stereochemistry,[15] while in the epoxidation of $\Delta^{8(14)}$- and in reactions of Δ^7-13-*epi*-pimarenes the observed products are derived only from the steric feasibility of the attack from the α- and β-face of the double bond. The evolution of boranes initially formed in the hydroboration–oxidation of $\Delta^{8(14)}$-13-*epi*-pimarenes is consistent with the appearance of small amounts of 7-hydroxy derivatives in the reaction product, derived from the positional isomerization of intermediate boranes.

The controlling factor must be the high degree of crowding around C-14 that would destabilize these intermediate boranes, leading to exchange among them. The equilibrium of hydroboration intermediates, favoured if there is a large excess of borane reagent, is able to reverse the stereochemistry of crowded to less hindered boranes, as has been described in the quantitative transformations of pinanylboranes.[16] In the case of $\Delta^{8(14)}$-13-*epi*-pimarenes the stability of the intermediate borane **20** must be much lower than that of its diastereoisomer **21** because it has a very important crowding on C-14 and very severe non-bonding interactions with Me(20).



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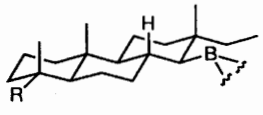

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This proposal agrees with the observed change in the stereochemistry of products obtained in the hydroboration of methyl isopimarate **11**.[17] This compound was hydroborated in 3 h to give 7,16-diols in a 3.5:1 relative yield of products resulting from α/β attack. However, when the reaction mixture was kept for 65 h at room temperature not only was the carboxylic ester at C-18 reduced to the corresponding alcohol, but also the relative yield of products with α- and β-stereochemistry was reversed to 1:4.7.

Thus, the β-stereospecificity can be explained as a result of the thermodynamic equilibration between diastereoisomers **20** and **21**, clearly favourable to the most stable stereoisomer **21**, under the conditions required for the hydroboration of 13-*epi*-pimar-8(14)-enes. With the more voluminous thexylborane, reflux is required for several hours to obtain a partial conversion; under such conditions only β isomers derived from positional and stereochemical equilibration were obtained.

In some instances compound **7**, apparently resulting from the *trans* addition to the double bond, was observed in up to 10% yield. Its structure was well established in the light of NMR data and the chemical transformations depicted in Scheme 1, although its formation cannot be explained by the generally accepted mechanism for hydroboration–oxidation.

* Tetrahydrofuran = THF.

Experimental

IR spectra were measured using a Beckmann (Acculab VIII) spectrometer for solutions (4%) in $CHCl_3$. NMR spectra were recorded on a Bruker WP200SY spectrometer (200 MHz for ^1H and 50.3 MHz for ^{13}C) for samples in $CDCl_3$ solution. Chemical shifts are reported in ppm from internal $SiMe_4$ and *J* values are given in Hz. Optical rotations (units 10^{-1} deg cm^2 g^{-1}) were measured on a Perkin-Elmer 241 digital polarimeter. Mass spectra were measured on a VG-TS-250 spectrometer (electronic impact 70 eV). Elemental analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyser.

Hydrogenation.—(a) *With* Pd/C. A solution of diene **1** (500 mg, 1.6 mmol) in EtOH (30 cm^3) containing Pd/C 10% (40 mg) was stirred for 15 min at 25 °C under H_2. The mixture was filtered, the solvent was evaporated off, and the residue was purified by chromatography [hexane–EtOAc (95:5)] to obtain monoene **3** (472 mg, 94%).

(b) *With* PtO_2. A solution of diene **1** (1.02 g, 3.2 mmol) and EtOH (20 cm^3) containing PtO_2 (35 mg) was stirred for 1 h at 25 °C under H_2. After usual work-up and chromatography [hexane–EtOAc (95:5)], compound **3** (1.02 g, 99%) was obtained.

In the same way diene **2** (1.2 g, 3.6 mmol) was hydrogenated to give monoene **4** (1.2 g, 99%), and diene **11** (0.6 g, 1.9 mmol) gave monoene **12** (0.6 g, 99%).

Methyl 15,16-dihydro-13-*epi*-pimar-8(14)-en-18-oate **3**. M.p. 52 °C (from hexane–EtOAc); $[\alpha]^{20}(\lambda)$ +13.6 (589), +14.3 (578), +16.5 (546), +291 (436) and +42.5 (365) (*c* 0.97 in $CHCl_3$); ν_{max}(film)/cm^{-1} 1740 and 1040; δ_H 0.79 (3 H, t, *J* 7.5, 16-H_3), 0.81 (3 H, s, 17-H_3), 0.89 (3 H, s, 20-H_3), 1.20 (3 H, s, 19-H_3), 3.64 (3 H, s, OMe) and 5.17 (1 H, s, 14-H); δ_C 38.4 (C-1), 18.2 (C-2), 37.0 (C-3), 47.5 (C-4), 49.2 (C-5), 24.8 (C-6), 35.3 (C-7), 135.7 (C-8), 51.3 (C-9), 37.5 (C-10), 18.9 (C-11), 33.6 (C-12), 33.8 (C-13), 131.4 (C-14), 36.3 (C-15), 8.1 (C-16), 25.5 (C-17), 179.2 (C-18), 17.0 (C-19), 15.0 (C-20) and 51.7 (OMe); *m/z* 318 (M$^+$, 57%), 302 (60), 289 (26) and 121 (100).

15,16-Dihydro-13-*epi*-pimar-8(14)-en-18-yl acetate **4**. Oil, $[\alpha]^{20}(\lambda)$ +27.1 (589), +28.2 (578), +32.3 (546), +58.8 (436) and +100.5 (365) (*c* 0.78 in $CHCl_3$); ν_{max}/cm^{-1} 1730, 1140 and 1070; δ_H 0.79 (3 H, t, *J* 7.5, 16-H_3), 0.82 (3 H, s, 17-H_3), 0.87 (3 H, s, 19-H_3), 0.89 (3 H, s, 20-H_3), 2.03 (3 H, s, OAc), 3.64 (1 H, d, *J* 10.8, 18-H), 3.86 (1 H, d, *J* 10.8, 18-H) and 5.17 (1 H, s, 14-H); δ_C 38.9 (C-1), 18.2 (C-2), 36.4 (C-3), 36.7 (C-4), 48.9 (C-5), 22.6 (C-6), 35.6 (C-7), 135.8 (C-8), 51.4 (C-9), 37.9 (C-10), 19.1 (C-11), 33.7 (C-12), 36.4 (C-13), 131.3 (C-14), 36.1 (C-15), 8.1 (C-16), 25.5 (C-17), 73.1 (C-18), 17.9 (C-19), 15.3 (C-20), 20.8 (OCO*Me*), 170.9 (O*C*OMe); *m/z* 330 (M$^+$, 80%), 257 (98), 135 (100) and 121 (52).

Methyl 15,16-dihydro-13-*epi*-pimar-7-en-18-oate **12**. Oil, $[\alpha]^{20}(\lambda)$ −3.9 (589), −4.3 (578), −4.9 (546), −8.7 (436) and −10.1 (365) (*c* 1.13 in $CHCl_3$); ν_{max}(film)/cm^{-1} 1740 and 1040; δ_H 0.81 (3 H, t, *J* 7.3, 16-H_3), 0.69 (3 H, s, 17-H_3), 0.88 (3 H, s, 20-H_3), 1.26 (3 H, s, 19-H_3), 3.63 (3 H, s, OMe) and 5.28 (1 H, br s, 14-H); δ_C 39.0 (C-1), 18.1 (C-2), 37.2 (C-3), 46.8 (C-4), 45.5 (C-5), 25.3 (C-6), 120.4 (C-7), 136.6 (C-8), 52.6 (C-9), 35.2 (C-10), 20.3 (C-11), 37.6 (C-12), 33.5 (C-13), 36.4 (C-14), 37.5 (C-15), 7.7 (C-16), 21.1 (C-17), 179.2 (C-18), 17.4 (C-19), 15.3 (C-20) and 51.9 (OMe); *m/z* 318 (M$^+$, 57%), 302 (60), 289 (25), 258 (75) and 121 (100).

Hydroboration (*Temperature and Time as in Table 1*).—(a) *With* 1 mol dm^{-3} BH_3·THF.* (Entry 1) BH_3·THF (1 mol dm^{-3}; 6 cm^3) was added under N_2 at 0 °C to a solution of compound **3** (300 mg, 0.95 mmol) in THF (13 cm^3). The mixture was kept for 1 h at 0 °C, then for 8 h at 25 °C. EtOH (15 cm^3), 3 mol dm^{-3} NaOH (4 cm^3) and 33% H_2O_2 (4 cm^3) were slowly added at 0 °C and the mixture was stirred at 50 °C for 1 h. After addition

of EtOAc and NaCl the organic layer was washed with water, dried, and evaporated to give the reaction product (325 mg). Flash chromatography [hexane–EtOAc (9:1 and 8:2)] gave compounds **5** (181 mg, 57%), **7** (31.1 mg, 10%) and **6** (27.6 mg, 10%).

Methyl 15,16-*dihydro*-14β-*hydroxy*-13-epi-*pimaran*-18-*oate* **5**. M.p. 118 °C (from hexane–EtOAc) (Found: C, 74.85; H, 11.0. $C_{21}H_{36}O_3$ requires C, 75.00; H, 10.71%); $[\alpha]^{20}(\lambda)$ −7.8 (589), −8.1 (578), −9.1 (546) and −14.4 (436) (*c* 1.49 in $CHCl_3$); ν_{max}/cm^{-1} 3610, 1720, 1100 and 1000; δ_H 0.81 (3 H, t, *J* 7.5, 16-H_3), 0.81 (3 H, s, 17-H_3), 0.88 (3 H, s, 20-H_3), 1.17 (3 H, s, 19-H_3), 2.90 (1 H, d, *J* 10.8, 14-H) and 3.65 (3 H, s, OMe); δ_C 38.3 (C-1), 18.2 (C-2), 37.0 (C-3), 47.8 (C-4), 49.7 (C-5), 24.0 (C-6), 31.2 (C-7), 38.6 (C-8), 54.6 (C-9), 36.3 (C-10), 19.5 (C-11), 34.2 (C-12), 37.5 (C-13), 81.4 (C-14), 33.7 (C-15), 7.6 (C-6), 16.8 (C-17), 179.4 (C-18), 16.8 (C-19), 14.6 (C-20) and 51.8 (OMe); *m/z* 336 (M^+, 8%), 318 (39), 289 (58), 259 (58), 218 (100), 189 (56) and 121 (42). Acetate **8**, m.p. 87 °C (from hexane); $[\alpha]^{20}(\lambda)$ +6.9 (589), +7.2 (578), +8.6 (546) and +15.0 (436) (*c* 1.49 in $CHCl_3$); ν_{max}/cm^{-1} 1725, 1190 and 1040; δ_H 0.78 (3 H, t, *J* 7.5, 16-H_3), 0.86 (3 H, s, 17-H_3), 0.89 (3 H, s, 20-H_3), 1.16 (3 H, s, 19-H_3), 2.04 (3 H, s, OAc), 3.62 (3 H, s, OMe) and 4.50 (1 H, d, *J* 10.2, 14-H); δ_C 38.2 (C-1), 18.1 (C-2), 36.8 (C-3), 47.6 (C-4), 49.3 (C-5), 23.7 (C-6), 30.4 (C-7), 36.8 (C-8), 54.4 (C-9), 36.3 (C-10), 19.3 (C-11), 34.0 (C-12), 37.2 (C-13), 82.6 (C-14), 33.4 (C-15), 7.3 (C-16), 17.3 (C-17), 179.1 (C-18), 16.7 (C-19), 14.5 (C-20), 51.8 (OMe), 20.8 (OCO*Me*) and 170.9 (O*C*OMe); *m/z* 318 (M^+ − HOAc, 59%), 289 (100), 259 (95), 229 (28), 189 (38) and 121 (67).

Methyl 15,16-*dihydro*-14α-*hydroxy*-13-epi-*pimaran*-18-*oate* **7**. M.p. 104 °C (from hexane) (Found: C, 74.8; H, 11.2%); $[\alpha]^{20}(\lambda)$ +0.12 (589), +0.12 (578), +0.25 (546) and +1.25 (436) (*c* 0.80 in $CHCl_3$); ν_{max}/cm^{-1} 3600, 1720, 1100 and 1010; δ_H 0.81 (3 H, t, *J* 7.2, 16-H_3), 0.82 (3 H, s, 17-H_3), 0.88 (3 H, s, 20-H_3), 1.18 (3 H, s, 19-H_3), 3.19 (1 H, br s, 14-H) and 3.64 (3 H, s, OMe); δ_C 38.4 (C-1), 18.2 (C-2), 37.0 (C-3), 48.7 (C-4), 48.2 (C-5), 24.4 (C-6), 29.7 (C-7), 35.9 (C-8), 49.5 (C-9), 36.3 (C-10), 19.8 (C-11), 32.8 (C-12), 38.4 (C-13), 76.3 (C-14), 30.5 (C-15), 7.3 (C-16), 20.1 (C-17), 179.4 (C-18), 17.0 (C-19), 14.4 (C-20) and 51.8 (OMe); *m/z* 318 ($M^+ - H_2O$, 69%), 289 (47), 259 (57), 203 (99), 189 (95), 180 (75) and 121 (100).

15,16-*Dihydro*-13-epi-*pimarane*-14β,18-*diol* **6**. M.p. 182 °C (from hexane–Et_2O) (Found: C, 77.9; H, 11.9. $C_{20}H_{36}O_2$ requires C, 77.92; H, 11.69%); $[\alpha]^{20}(\lambda)$ −19.0 (589), −19.9 (578), −22.3 (546), −36.3 (436) and −54.5 (365) (*c* 0.71 in EtOH); ν_{max}(KBr 1%)/cm^{-1} 3300, 1080, 1060, 1020, 980 and 810; δ_H 0.78 (3 H, s, 19-H_3), 0.82 (3 H, t, *J* 7.5, 16-H_3), 0.82 (3 H, s, 17-H_3), 0.89 (3 H, s, 20-H_3), 2.90 (1 H, d, *J* 9.8, 14-H), 3.10 (1 H, d, *J* 10.9, 18-H) and 3.39 (1 H, d, *J* 10.9, 18-H); δ_C 38.8 (C-1), 18.3 (C-2), 35.5 (C-3), 36.6 (C-4), 48.4 (C-5), 21.2 (C-6), 31.3 (C-7), 38.4 (C-8), 54.6 (C-9), 37.5 (C-10), 19.7 (C-11), 34.3 (C-12), 37.5 (C-13), 81.6 (C-14), 33.8 (C-15), 7.5 (C-16), 16.8 (C-17), 72.3 (C-18), 17.7 (C-19) and 14.9 (C-20); *m/z* 308 (M^+, 5%), 277 (98) and 259 (100). Diacetate **9**. Oil, $[\alpha]^{20}(\lambda)$ +5.5 (589), +5.2 (578), +5.9 (546), +11.2 (436) and +20.0 (365) (*c* 0.66 in $CHCl_3$); ν_{max}(film)/cm^{-1} 1730, 1720, 1040 and 980; δ_H 0.78 (3 H, t, *J* 7.5, 16-H_3), 0.83 (3 H, s, 19-H_3), 0.86 (3 H, s, 17-H_3), 0.90 (3 H, s, 20-H_3), 2.05 (6 H, s, OAc), 3.58 (1 H, d, *J* 11.0, 18-H), 3.82 (1 H, d, *J* 11.0, 18-H) and 4.50 (1 H, d, *J* 10.2, 14-H); δ_C 38.4 (C-1), 17.9 (C-2), 35.7 (C-3), 36.4 (C-4), 48.4 (C-5), 20.7 (C-6), 30.4 (C-7), 36.4 (C-8), 54.2 (C-9), 36.4 (C-10), 19.3 (C-11), 33.9 (C-12), 37.0 (C-13), 82.5 (C-14), 33.2 (C-15), 7.2 (C-16), 17.2 (C-17), 72.4 (C-18), 17.5 (C-19), 14.5 (C-20), 20.7 (OCO*Me*) and 170.8 (O*C*OMe); *m/z* 332 (M^+ − HOAc, 58%), 301 (20), 259 (100) and 163 (30).

(Entries 2–5). Under conditions stated in Table 1 and after usual work-up the following results were obtained: Entry 2; from **4** (1.09 g, 3.3 mmol) only product **6** (890 mg, 88%). Entry 4; from **4** (440 mg, 1.3 mmol) diols **6** (185.5 mg, 40%) and **16** (69.6 mg, 15%). Entry 5; from **12** (0.6 g, 1.9 mmol) a mixture of hydroxy esters **13** + **14** (140 mg, 22%), **14** (342 mg, 54%) and **16** (23 mg, 4%).

Methyl 15,16-dihydro-7β-hydroxy-13-*epi*-pimaran-18-oate **13**. (Spectral data from a mixture **13** + **14**), δ_H 0.81 (3 H, s, 17-H_3), 0.82 (3 H, t, *J* 7.5, 16-H_3), 0.91 (3 H, s, 20-H_3), 1.09 (3 H, s, 19-H_3), 3.20 (1 H, ddd, *J* 6.2, 9.2, 9.5, 7-H) and 3.64 (3 H, s, OMe); δ_C 38.1 (C-1), 18.1 (C-2), 37.0 (C-3), 47.4 (C-4), 46.7 (C-5), 33.9 (C-6), 76.0 (C-7), 39.7 (C-8), 54.0 (C-9), 36.1 (C-10), 20.2 (C-11), 41.7 (C-12), 32.6 (C-13), 37.0 (C-14), 38.4 (C-15), 7.7 (C-16), 21.6 (C-17), 179.1 (C-18), 16.6 (C-19), 14.7 (C-20) and 51.7 (OMe).

Methyl 15,16-*dihydro*-7α-*hydroxy*-8,13-*di*-epi-*pimaran*-18-*oate* **14**. M.p. 81 °C (from hexane–EtOAc) (Found: C, 74.7; H, 11.15. $C_{21}H_{36}O_3$ requires C, 75.00; H, 10.71%); $[\alpha]^{20}(\lambda)$ −9.4 (589), −9.9 (578), −11.0 (546), −17.0 (436) and −23.6 (365) (*c* 1.1 in $CHCl_3$); ν_{max}/cm^{-1} 3610, 1720 and 1100; δ_H 0.76 (3 H, t, *J* 7.6, 16-H_3), 0.80 (3 H, s, 20-H_3), 1.08 (3 H, s, 17-H_3), 1.19 (3 H, s, 19-H_3), 3.66 (3 H, s, OMe) and 3.71 (1 H, br s, 7-H); δ_C 39.7 (C-1), 17.7 (C-2), 37.2 (C-3), 46.9 (C-4), 41.1 (C-5), 28.4 (C-6), 73.1 (C-7), 38.9 (C-8), 43.1 (C-9), 38.7 (C-10), 20.4 (C-11), 38.6 (C-12), 32.5 (C-13), 34.7 (C-14), 29.5 (C-15), 7.9 (C-16), 29.1 (C-17), 179.2 (C-18), 16.7 (C-19), 18.9 (C-20) and 51.8 (OMe); *m/z* 318 ($M^+ - H_2O$, 92%), 259 (100), 189 (28) and 123 (93). Acetate **15**. Oil, ν_{max}/cm^{-1} 1730, 1720 and 1080; δ_H 0.76 (3 H, t, *J* 7.5, 16-H_3), 0.82 (3 H, s, 20-H_3), 1.09 (3 H, s, 17-H_3), 1.17 (3 H, s, 19-H_3), 2.06 (OAc), 3.61 (3 H, s, OMe) and 4.67 (1 H, br s, 7-H); δ_C 39.4 (C-1), 17.7 (C-2), 37.6 (C-3), 46.9 (C-4), 42.1 (C-5), 25.7 (C-6), 76.2 (C-7), 36.3 (C-8), 43.4 (C-9), 38.2 (C-10), 20.0 (C-11), 36.8 (C-12), 32.2 (C-13), 34.3 (C-14), 28.1 (C-15), 7.6 (C-16), 28.5 (C-17), 178.5 (C-18), 16.4 (C-19), 18.6 (C-20) and 51.4 (OMe).

15,16-*Dihydro*-8,13-*di*-epi-*pimarane*-7α,18-*diol* **16**. (Found: C, 77.8; H, 12.0. $C_{20}H_{36}O_2$ requires C, 77.92; H, 11.69%); ν_{max}(KBr 1%)/cm^{-1} 3300, 1080, 1060 and 1020; δ_H 0.69 (3 H, s, 19-H_3), 0.76 (3 H, t, *J* 7.6, 16-H_3), 0.81 (3 H, s, 20-H_3), 1.14 (3 H, s, 17-H_3), 2.92 (1 H, d, *J* 10.9, 18-H), 3.45 (1 H, d, *J* 10.9, 18-H) and 3.75 (1 H, br s, 7-H); δ_C 40.4 (C-1), 18.0 (C-2), 35.4 (C-3), 38.9 (C-4), 39.5 (C-5), 26.0 (C-6), 73.6 (C-7), 38.9 (C-8), 43.2 (C-9), 37.1 (C-10), 20.7 (C-11), 39.1 (C-12), 32.6 (C-13), 34.7 (C-14), 28.5 (C-15), 8.0 (C-16), 29.2 (C-17), 71.3 (C-18), 18.1 (C-19) and 19.4 (C-20); *m/z* 288 ($M^+ - H_2O$, 10%), 259 (100) and 189 (50). Diacetate **17**. Oil, ν_{max}/cm^{-1} 1730, 1720 and 1030; δ_H 0.78 (3 H, t, *J* 7.6, 16-H_3), 0.81 (3 H, s, 20-H_3), 0.85 (3 H, s, 19-H_3), 1.12 (3 H, s, 17-H_3), 2.03 (3 H, s, OAc), 2.05 (3 H, s, OAc), 3.65 (1 H, d, *J* 10.7, 18-H), 3.78 (1 H, d, *J* 10.7, 18-H) and 4.76 (1 H, br s, 7-H); δ_C 40.0 (C-1), 17.9 (C-2), 35.8 (C-3), 36.2 (C-4), 42.0 (C-5), 24.0 (C-6), 77.3 (C-7), 36.1 (C-8), 43.7 (C-9), 38.0 (C-10), 20.5 (C-11), 38.7 (C-12), 32.6 (C-13), 34.6 (C-14), 28.7 (C-15), 7.9 (C-16), 29.1 (C-17), 72.8 (C-18), 17.6 (C-19), 19.1 (C-20), 21.0 (OCO*Me*), 21.6 (OCO*Me*), 170.3 (O*C*OMe) and 170.7 (O*C*OMe).

(b) *With BBN*. A solution of compound **4** in dry THF was added to a stirred solution of BBN in THF at 0 °C under N_2. The mixture was kept as indicated in Table 1 (Entries 6–7). After treatment (H_2O_2) and usual work-up, unchanged substrate **4** was recovered.

(c) *With thexylborane*. (Entry 8, Table 1). A solution of substrate **4** (400 mg, 1.2 mmol) in THF (3 cm^3) was added dropwise under N_2 to a freshly prepared thexylborane solution (4 mmol).[18] After reaction, oxidation (H_2O_2) and usual work-up, unchanged substrate **4** (400 mg) was recovered.

(Entry 9). When the reaction was carried out under reflux for 42 h, compounds **6** (55.3 mg, 15%) and **18** (25.8 mg, 7%), which was purified as its diacetate **19**, were obtained.

15,16-Dihydro-13-*epi*-pimarane-7β,18-diol **18**. Oil, ν_{max}/cm^{-1} 3300, 1100 and 1020; δ_H 0.79 (3 H, s, 17-H_3), 0.82 (3 H, t, *J* 7.5, 16-H_3), 0.82 (3 H, s, 19-H_3), 0.92 (3 H, s, 20-H_3), 3.08 (1 H, d, *J* 10.9, 18-H), 3.20 (1 H, ddd, *J* 5.1, 10.0, 10.2, 7-H) and 3.36 (1 H, d, *J* 10.9, 18-H); δ_C 39.1 (C-1), 18.1 (C-2), 37.0 (C-3), 37.6 (C-4), 45.0 (C-5), 31.2 (C-6), 76.6 (C-7), 39.7 (C-8), 54.0 (C-9), 36.4 (C-10), 20.5 (C-11), 41.8 (C-12), 32.4 (C-13), 35.3 (C-14), 38.9 (C-15), 7.9 (C-16), 21.7 (C-17), 71.5 (C-18), 17.7 (C-19) and 15.0 (C-20). Diacetate **19**. Oil, $[\alpha]^{20}(\lambda)$ +22.3 (589), +22.9 (578), +26.5 (546), +45.6 (436) and +71.2 (365) (*c* 0.73 in $CHCl_3$); ν_{max}/cm^{-1} 1730, 1720 and 1190; δ_H 0.78 (3 H, t, *J* 7.5, 16-H_3), 0.80 (3 H, s, 17-H_3), 0.85 (3 H, s, 19-H_3), 0.93 (3 H, s, 20-H_3), 2.04 (3 H, s, OAc), 2.07 (3 H, s, OAc), 3.67 (1 H, d, *J* 11.0, 18-H), 3.75 (1 H, d, *J* 11.0, 18-H) and 4.45 (1 H, ddd, *J* 5.0, 9.2, 10.4, 7-H); δ_C 38.4 (C-1), 18.1 (C-2), 36.7 (C-3), 36.4 (C-4), 46.3 (C-5), 27.7 (C-6), 78.3 (C-7), 36.5 (C-8), 54.0 (C-9), 36.4 (C-10), 20.4 (C-11), 41.3 (C-12), 32.4 (C-13), 36.0 (C-14), 38.2 (C-15), 7.6 (C-16), 21.6 (C-17), 72.7 (C-18), 17.7 (C-19), 14.8 (C-20), 20.9 (OCO*Me*), 21.2 (OCO*Me*), 170.6 (O*C*OMe) and 171.1 (O*C*OMe); *m/z* 332 (M^+ − HOAc, 60%), 259 (100) and 189 (30).

Oxidations and Reductions.—(a) *Oxidation with Jones reagent.* A stirred solution of the alcohol in acetone (10 cm^3) at 0 °C was titrated with Jones reagent (CrO_3/H_2SO_4) until the orange colour persisted. After usual work up, compound **5** (80 mg) gave ketone **10** (80 mg, 100%) and compound **7** (30 mg) gave ketone **10** (28 mg, 99%).

Methyl 15,16-*dihydro*-14-*oxo*-13-epi-*pimaran*-18-*oate* **10**. M.p. 63 °C (from hexane–CH_2Cl_2) (Found: C, 75.2; H, 10.3. $C_{20}H_{36}O_2$ requires C, 75.40; H, 10.28%); $[\alpha]^{20}(\lambda)$ −23.4 (589), −25.0 (578), −30.5 (546) and −77.5 (436) (*c* 0.56 in $CHCl_3$); ν_{max}(film)/cm^{-1} 1725, 1700, 1250 and 1070; δ_H 0.81 (3 H, t, *J* 7.4, 16-H_3), 0.99 (3 H, s, 20-H_3), 1.09 (3 H, s, 17-H_3), 1.18 (3 H, s, 19-H_3), 1.44 (2 H, q, *J* 7.4, 15-H_2), 2.44 (1 H, ddd, *J* 4.1, 11.3, 12.1, 8-H) and 3.64 (3 H, s, OMe); δ_C 38.2 (C-1), 18.2 (C-2), 36.9 (C-3), 47.5 (C-4), 48.9 (C-5), 23.4 (C-6), 26.5 (C-7), 45.0 (C-8), 56.9 (C-9), 36.8 (C-10), 19.7 (C-11), 36.2 (C-12), 47.0 (C-13), 216.4 (C-14), 30.5 (C-15), 8.2 (C-16), 22.7 (C-17), 178.9 (C-18), 16.7 (C-19), 14.1 (C-20) and 51.7 (OMe).

A solution of compound **10** (15 mg) in KOH–MeOH 5% (3 cm^3) was maintained for 5 h at room temperature. After usual work-up only unchanged **10** was recovered.

(b) *Reduction with* $NaBH_4$. $NaBH_4$ (31 mg, 0.8 mmol) was slowly added under N_2 to a solution of compound **10** (100 mg, 0.3 mmol) in EtOH (12 cm^3). The mixture was stirred for 80 min at 25 °C. After the usual work-up, crude product was subjected to flash chromatography [hexane–EtOAc (95:5, 90:10 and 80:20)] to yield (in elution order): unchanged substrate **10** (20 mg, 20%), and products **7** (15 mg, 15%) and **5** (52 mg, 50%).

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