Calciferol and its Relatives. Part 20.[1] A Synthesis of Windaus and Grundmann's C_{19} Ketone

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Starting from 1β-[(*R*)-2-hydroxy-1-methylethyl]-7aβ-methyl-3aα,6,7,7aβ-tetrahydroindane (1) † syntheses have been effected of two bicyclic compounds suitable as intermediates for conversion into vitamin D-active products, *viz.* Windaus and Grundmann's ketone (20) {7aβ-methyl-1β-[(1*R*,4*R*)-1,4,5-trimethylhex-*trans*-2-enyl]-3aα,4,5,6,-7,7aβ-hexahydroindan-4-one}, and des-AB-cholestane-8β,25-diol (23) {4β-hydroxy-1β-[(*R*)-5-hydroxy-1,5-dimethylhexyl]-7aβ-methyl-3aα,4,5,6,7,7aβ-hexahydroindane}.

THE optically active hydrindenylpropanol (1) † described in Part 19 [1] was intended as an intermediate for the synthesis of des-AB-cholestane derivatives which could in turn be transformed into vitamin D-active compounds. The present paper describes the conversion of the hydrindenylpropanol (1) into two such intermediates; first, the C_{19} ketone (20), which Windaus and Grundmann [2] obtained by oxidative degradation of vitamin D_2, and which was of interest to us for a synthesis of that vitamin; and secondly, des-AB-cholestane-8β,25-diol (23), intended as an intermediate for the synthesis of 25-hydroxyvitamin D_3 and its relatives.

Our intended routes to both the compounds (20) and (23) entailed mono-protected derivatives of the diol (5), and, with the object of simplifying their preparation, we first converted the alcohol (1) into its benzyl ether. Addition of acetyl hypobromite, followed by treatment with alkali, gave the β-epoxide (3), which was reduced with lithium aluminium hydride to the 8β-alcohol (4). Hydrogenolytic removal of the benzyl group then gave the known [3] diol (5). Benzoylation of the 8β-alcohol (4), followed by removal of the benzyl group, would clearly give the monobenzoate (7), which we required for our work. In practice, the difference in reactivity between the two hydroxy groups in the diol (5) is so great that the use of the diol itself proved just as convenient as that of the benzyl ether (4). Thus, reaction with an excess of benzoyl chloride gave the diol dibenzoate, which when treated at room temperature with ethanolic 0.55N-potassium hydroxide gave the secondary monobenzoate (7) in *ca.* 95% yield. Similarly, reaction of the diol (5) with 1 mol. equiv. of toluene-*p*-sulphonyl chloride in pyridine gave almost exclusively the primary tosylate (6), which we required for the synthesis of the diol (23).

Oxidation of the monobenzoate (7) with Collins'

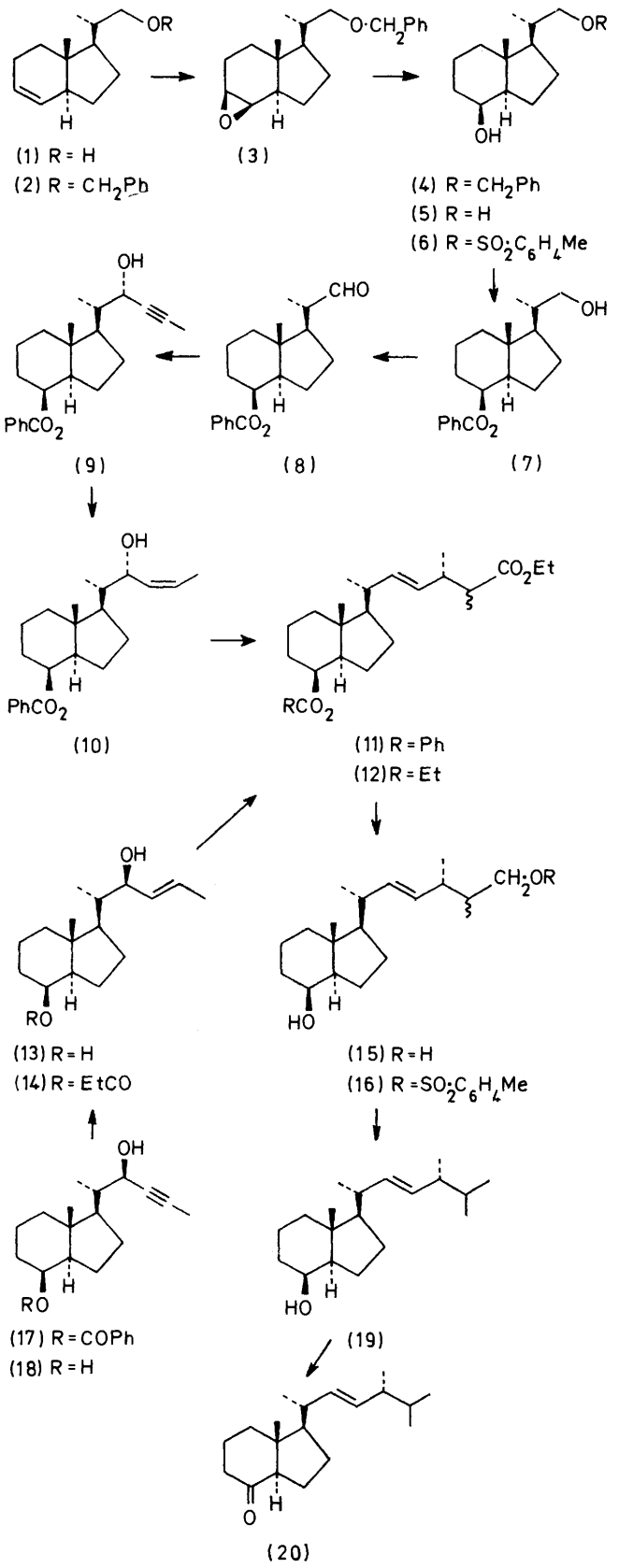
† All the structures in this paper represent absolute configurations.

[1] Part 19, C. B. Chapleo, P. Hallett, B. Lythgoe, I. Waterhouse, and P. W. Wright, *J.C.S. Perkin I*, 1977, 1211.

[2] A. Windaus and W. Grundmann, *Annalen*, 1936, **524**, 295.

[3] H. H. Inhoffen, G. Quinkert, S. Schütz, G. Friedrich, and E. Tober, *Chem. Ber.*, 1958, **91**, 781.

[4] W. Sucrow and B. Girgensohn, *Chem. Ber.*, 1970, **103**, 750; W. Sucrow, B. Schubert, W. Richter, and M. Slopianka, *ibid.*, 1971, **104**, 3689; W. Sucrow, P. P. Caldeira, and M. Slopianka, *ibid.*, 1973, **106**, 2236.



reagent gave the aldehyde (8). Intact steroidal analogues of (8) have been used by Sucrow [4] for the construction of derivatives with side-chains related to that of ergosterol; his methods, which permit control of the configuration at C-24 and also provide the desired *trans*-geometry of the 22-double bond, were used here in slightly modified form.

The aldehyde (8) reacted with propynylmagnesium bromide to give a mixture of the acetylenic alcohols (9) and (17), which were separated by chromatography. One of them formed a crystalline *p*-nitrobenzoate; analogy [4] suggested that this, the less polar of the two alcohols, was probably the 22*S*-compound (9), and this proved correct.

Semihydrogenation of the alcohol (9) with Lindlar catalyst gave the *cis*-allylic alcohol (10), which reacted with ethyl orthopropionate in a Claisen rearrangement to give in good yield a mixture of the two esters (11), as was apparent from the ^{1}H n.m.r. spectrum of the product. These isomers differ in configuration at C-25; * both possess the 24*R*-configuration, which is predetermined by the initial C-22 configuration, the *cis*-geometry of the allyl double bond, and the preferred chair geometry of the rearrangement transition-state. The mixed esters (11) were reduced to the diols (15), which reacted selectively with toluene-*p*-sulphonyl chloride in pyridine to give the 26-monotosylates (16). These on treatment with lithium aluminium hydride gave a single alcohol (19). The alcohol formed a crystalline 3,5-dinitrobenzoate, which proved identical with that of des-AB-ergost-22-en-8β-ol [3] obtained by reduction of the Windaus–Grundmann ketone (20). This ketone is easily obtained from the alcohol (19) by oxidation with chromic oxide and pyridine.

The 22*R*-compound (17) did not crystallise, but the corresponding acetylenic diol (18) was crystalline, and so also was the *trans*-ethylenic diol (13), obtained by reducing the benzoate (17) with lithium aluminium hydride.[5] Selective hydrolysis of the dipropionate of the diol (13) gave the 8-monopropionate (14) without difficulty, and this reacted with ethyl orthopropionate to give the diesters (12). These mixed diesters were treated in the same way as the diesters (11) in order to convert the ethoxycarbonyl group into a methyl group; they provided the single alcohol (19) in the expected manner, and thus this alcohol was obtained from both the diastereoisomers (9) and (17).

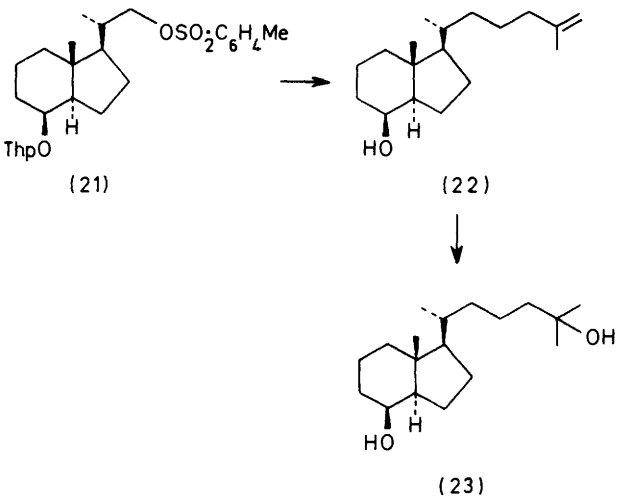
Our projected route to the 8β,25-diol (23) was influenced by recent experiments which have demonstrated the efficiency of coupling reactions between primary tosylates and Grignard reagents in the presence of dilithium tetrachlorocuprate.[6] The tosylate (6),

* Steroidal numbering.

[5] J. D. Chanley and H. Sobotka, *J. Amer. Chem. Soc.*, 1949, **71**, 4140; J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Janson, and T. Walker, *J. Chem. Soc.*, 1952, 1094.

[6] M. Tamura and J. Kochi, *Synthesis*, 1971, 303; G. Fouquet and M. Schlosser, *Angew. Chem. Internat. Edn.*, 1974, **13**, 82; M. Schlosser, *ibid.*, p. 701.

protected as its tetrahydropyranyl derivative (21), was allowed to react in the presence of this cuprate with 3-methylbut-3-enylmagnesium chloride, and the protecting group was then removed to give, in good yield, the unsaturated alcohol (22). This was characterised as the



crystalline 3,5-dinitrobenzoate, and its structure was confirmed by conversion by hydrogenation into des-AB-cholestan-8β-ol, which was also characterised as the 3,5-dinitrobenzoate. Markownikoff hydration of the terminal olefin (22) by Brown's method [7] gave in excellent yield the crystalline diol (23).

EXPERIMENTAL

N.m.r. data (90 MHz) refer to solutions in $CDCl_3$, and $[\alpha]_D$ values to solutions in $CHCl_3$. T.l.c. and p.l.c. were carried out with Kieselgel GF_{254}. Light petroleum refers to the fraction b.p. 60—80 °C, unless otherwise specified.

Conversion of the Hydrindenylpropanol (1) *into the Diol* (5).—A vigorously stirred mixture of the alcohol (1) (140 mg), benzyl chloride (1 g), and powdered potassium hydroxide (600 mg) in dry benzene (25 cm³) was heated under reflux with azeotropic removal of water for 13½ h. Water was added to the cooled mixture, and the product, isolated with ether, was purified by p.l.c. (15% benzene–light petroleum). The benzyl ether (2) (171 mg) had $\nu_{max.}$ (film) 675s, 695s, 735s, 1 095s, and 3 020w cm^{-1}, τ 4.42 (2 H, s, =CH–), 6.45—6.9 (2 H, m, CH_2·O), 8.89 (3 H, d, *J* 7 Hz, CH*Me*), and 9.28 (3 H, s, Me) (Found: M^+, 284.212 89. Calc. for $C_{20}H_{28}O$: *M*, 284.214 00). To the benzyl ether (171 mg) in carbon tetrachloride (5 cm³) at 0 °C a solution of acetyl hypobromite in carbon tetrachloride (0.1M; 16.8 cm³) was added with stirring during 10 min; stirring was continued at 0 °C for 45 min, after which the excess of reagent was destroyed with aqueous 10% sodium hydrogen sulphite. The carbon tetrachloride layer was separated, washed with water, dried, and evaporated to give the crude bromohydrin acetate (260 mg). This was stirred with potassium hydroxide (1.6 g) in ethanol (20 cm³) at 55 °C for 2 h; the cooled mixture was then neutralised with glacial acetic acid and evaporated under reduced pressure. The residue was partitioned between aqueous sodium hydrogen carbonate (40 cm³) and ether. Evaporation of the ether layer, chromatography on neutral alumina (grade III; 25 g), and elution with 25% benzene–light petroleum (b.p. 40—60 °C) gave the β-epoxide (3) (90 mg). The epoxide (85 mg) and lithium aluminium hydride (70 mg) were kept together in dry ether (10 cm³) at 20 °C for 1 h and then under reflux for 1 h. The cooled (0 °C) solution was then treated with ethyl acetate, followed by saturated aqueous sodium potassium tartrate (15 cm³). Isolation with ether gave the benzyloxy alcohol (4) as an oil (82 mg). This was hydrogenated over 5% palladised charcoal (50 mg) in ethanol (6 cm³) containing a little hydrochloric acid, after which normal work-up and p.l.c. (50% ethyl acetate–benzene) gave the diol (5) (33 mg) as needles [from ether–light petroleum (b.p. 40—60 °C)], m.p. 113—114°, alone or mixed with authentic material which had m.p. 114° (lit.,[3] m.p. 109—110°), $\nu_{max.}$ ($CHCl_3$) 3 460m and 3 630s cm^{-1}, τ 5.93br (1 H, s, $W_{\frac{1}{2}}$ 6 Hz, CH·O), 6.35 (1 H, dd, J_{gem} 11, J_{vic} 4 Hz, CH_2·O), 6.62 (1 H, dd, J_{gem} 11, J_{vic} 7 Hz, CH_2·O), 8.96 (3 H, d, *J* 6.5 Hz, CH*Me*), and 9.04 (3 H, s, Me).

The Monobenzoate (7).—The diol (5) was converted into its dibenzoate, a portion (4.2 g) of which was stirred at 20 °C with potassium hydroxide (1.7 g) in ethanol (50 cm³) and benzene (5 cm³). The mixture was acidified (Congo Red) with glacial acetic acid, solvents were removed under reduced pressure, and water (20 cm³) was added. Isolation with ether, and chromatography on silica gel gave the monobenzoate (7) as an oil (3.0 g), homogeneous to t.l.c., $\nu_{max.}$ (film) 1 275s, 1 715s, and 3 420s cm^{-1}, τ 1.95 (2 H, m, ArH), 2.6 (3 H, m, ArH), 4.6 br (1 H, s, CH·O), 6.33 (1 H, dd, J_{gem} 11, J_{vic} 4 Hz, CH_2·O), 6.62 (1 H, dd, J_{gem} 11, J_{vic} 6 Hz, CH_2·O), 8.93 (3 H, d, *J* 6 Hz, CH*Me*), and 8.93 (3 H, s, Me).

The Acetylenic Alcohols (9) *and* (16).—The monobenzoate (7) (1.97 g) in methylene chloride (20 cm³) was added to a stirred solution of Collins' reagent [from chromic oxide (6 g)] in methylene chloride (260 cm³). After 1 h the filtered solution was washed thoroughly with saturated aqueous sodium hydrogen carbonate, dried and evaporated. The residue was extracted with ether, and the filtered extract was evaporated to give the crude aldehyde (8) as an oil (1.75 g), $\nu_{max.}$ (film) 1 275s, 1 720s, and 2 720w cm^{-1}, τ 0.40 (d, *J* 4 Hz, CH=O).

To a stirred solution of propyne (8 cm³) in dry tetrahydrofuran (14 cm³) at −50 °C under nitrogen, ethylmagnesium bromide [from magnesium (787 mg)] in ether (13 cm³) was added; stirring was continued at −30 °C for ½ h, and the stirred mixture was then allowed to warm to 20 °C during 2 h. Benzene (10 cm³) was then added, and the mixture was stirred at 0 °C during the addition (10 min) of the aldehyde (8) (1.75 g) in tetrahydrofuran (10 cm³). Stirring was continued at 20 °C during ¾ h, and saturated aqueous ammonium chloride was added. Solvents were then removed under reduced pressure, water (20 cm³) was added, and the product, isolated with ether, was chromatographed on Kieselgel. Elution with benzene gave the less polar isomer (9) as an oil (650 mg), $\nu_{max.}$ (film) 1 275s, 1 715s, 2 220w, and 3 480s cm^{-1}, τ 8.14 (3 H, m, ≡CMe), 8.93 (3 H, d, *J* 6 Hz, CH*Me*), and 8.92 (3 H, s, CMe) (Found: M^+, 354.221 01. Calc. for $C_{23}H_{30}O_3$: *M*, 354.219 48). The *p-nitrobenzoate* of 4β-*benzoyloxy*-1β-[:1S,2S)-2-*hydroxy*-1-*methylpent*-3-*ynyl*]-7aβ-*methyl*-3aα,4,5,6,7,7aβ-*hexahydroindane* separated from light petroleum: m.p. 157—158.5°, $[\alpha]_D^{25}$ +30.1°, τ 8.12 (3 H, d, *J* 3 Hz, ≡CMe), 8.81 (3 H, d, *J* 7 Hz, CH*Me*), and 8.92 (3 H, s, CMe) (Found: C, 72.2; H, 6.5; N, 2.55. $C_{31}H_{33}NO_6$ requires C, 72.2; H, 6.45; N, 2.7%).

[7] H. C. Brown and P. Geoghegan, *J. Amer. Chem. Soc.*, 1967, **89**, 1522; *J. Org. Chem.*, 1970, **35**, 1844.

The more polar alcohol (17) was eluted from the chromatogram with 5% ethyl acetate in benzene; it formed an oil (480 mg), $\nu_{max.}$ (film) 1 275s, 1 715s, 2 220w, and 3 480s cm^{-1}, τ 8.18 (3 H, d, *J* 3 Hz, ≡CMe), 8.88 (3 H, d, *J* 7 Hz, CH*Me*), and 8.96 (3 H, s, CMe) (Found: M^+, 354.220 70. Calc. for $C_{23}H_{30}O_3$: *M*, 354.219 48). Hydrolysis with ethanolic potassium hydroxide gave 4β-*hydroxy*-1β-[(1S,2R)-2-*hydroxy*-1-*methylpent*-3-*ynyl*]-7aβ-*methyl*-3aα,4,5,6,7,7aβ-*hexahydroindane* (18), m.p. 135—136° (from chloroform–light petroleum), $[\alpha]_D^{25}$ +19.8°, $\nu_{max.}$ ($CHCl_3$) 1 460m and 3 400s cm^{-1}, τ 5.63br (1 H, s, ≡C–C*H*–OH), 5.90br (1 H, s, C*H*–OH), 8.12 (3 H, d, *J* 3 Hz, ≡CMe), 8.78 (3 H, d, *J* 7 Hz, CH*Me*), and 9.02 (3 H, s, CMe) (Found: C, 76.4; H, 10.35. $C_{16}H_{26}O_2$ requires C, 76.7; H, 10.5%).

Conversion of the Acetylenic Alcohol (9) *into the Alcohol* (19).—Semihydrogenation of the alcohol (9) over Lindlar catalyst in ethyl acetate, followed by chromatographic purification (silica gel; 5% ethyl acetate in benzene), gave the *cis*-allylic alcohol (10) as an oil, $\nu_{max.}$ (film) 1 275s, 1 720s, and 3 500s cm^{-1}, τ 8.26 (3 H, d, *J* 6 Hz, =CMe), 8.92 (3 H, s, CMe), and 8.95 (3 H, d, *J* 7 Hz, CH*Me*). A portion (90 mg) was heated under reflux in xylene (10 cm^3) with ethyl orthopropionate (200 mg) and propionic acid (50 mg) with continuous removal of ethanol. After 2½ h solvents were removed under reduced pressure, and the product was chromatographed on silica gel (benzene) to give the mixed esters (11) as an oil (87 mg), $\nu_{max.}$ 975m, 1 275s, and 1 720s cm^{-1}, τ 4.80 (2 H, m, =CH–), 5.86 and 5.89 (2 q, *J* 7 Hz, O·C*H*$_2$Me of two isomers), 8.74 (3 H, t, *J* 8 Hz, CH_2*Me*), and 8.93 (3 H, s, CMe).

Reduction of the above material in the usual way with lithium aluminium hydride in ether at 25 °C for 4 h gave an oily diol mixture (15) (60 mg), $\nu_{max.}$ (film) 975m and 3 330s cm^{-1}; this was kept in dry pyridine (2 cm^3) at 20 °C with toluene-*p*-sulphonyl chloride (100 mg) for 16 h after which the excess of reagent was decomposed with water, normal work-up then giving the monotosylates (16) (70 mg), $\nu_{max.}$ (film) 965s, 1 180s, 1 360s, 3 470s, and 3 575s cm^{-1}, τ 2.25 (2 H, d, *J* 12 Hz, ArH), 2.70 (2 H, d, *J* 12 Hz, ArH), 4.95 (2 H, m, =CH), 5.95br (1 H, s, CH·O), 5.7—6.25 (2 H, m, CH_2·OTs), 7.60 (3 H, s, Ar*Me*), and 9.0—9.3 (12 H, 4 CH_3). The monotosylates (70 mg) and lithium aluminium hydride (50 mg) were stirred together at 25 °C in ether (5 cm^3) for 3 h; N-NaOH (0.25 cm^3) was then added, followed by magnesium sulphate, and the solution was filtered and evaporated, giving the alcohol (19) (40 mg), which had the same R_F value and i.r. and n.m.r. spectra as authentic material obtained by degradation of vitamin D_2. The 3,5-dinitrobenzoate (67 mg), prepared in the usual way, formed plates (45 mg) (from light petroleum), m.p. 140—141°, undepressed on admixture with authentic material which had m.p. 140—141° (lit.,[3] 145°); $[\alpha]_D^{25}$ +69.2° (authentic material had $[\alpha]_D^{25}$ +69.2°); the n.m.r. spectra of the synthetic and authentic specimens were identical.

Conversion of the Acetylenic Alcohol (17) *into the Alcohol* (19).—The alcohol (17) (240 mg) and lithium aluminium hydride (100 mg) were heated together under reflux in tetrahydrofuran (10 cm^3) under nitrogen for 24 h. N-Sodium hydroxide (0.5 cm^3) was then added, followed by dry magnesium sulphate; filtration and evaporation gave an oil (170 mg) which was chromatographed on silica gel (5% ethyl acetate–benzene) to give 4β-*hydroxy*-1β-[(1S,2S)-2-*hydroxy*-1-*methylpent*-trans-3-*enyl*]-7aβ-*methyl*-3aα,4,5,6,7,7aβ-*hexahydroindane* (13), which separated from chloroform–light petroleum as rods (100 mg), m.p. 141—142°, $[\alpha]_D^{25}$ +11.5°, $\nu_{max.}$ ($CHCl_3$) 970m, 1 460s, and 3 400s cm^{-1}, τ 4.42 (2 H, m, =CH), 5.82br (1 H, s, =CH–C*H*–O), 5.92br (1 H, s, O·CH), 8.30 (3 H, d, *J* 5 Hz, =CH*Me*), and 9.08 (3 H, s, CMe) (Found: C, 76.4; H, 11.2. $C_{16}H_{28}O_2$ requires C, 76.1; H, 11.2%).

The diol (13) (55 mg) and propionic anhydride (250 mg) were heated together at 80 °C in dry pyridine (2 cm^3) for 4 days; normal work-up, followed by chromatography on silica gel (benzene), then gave the oily dipropionate (66 mg), $\nu_{max.}$ 970m, 1 190s, and 1 740s cm^{-1} (Found: M^+, 364.260 86. Calc. for $C_{22}H_{36}O_4$: *M*, 364.261 34). The dipropionate (100 mg) was kept at 20 °C with potassium hydroxide (150 mg) in ethanol (2 cm^3) for 20 h; after neutralisation with glacial acetic acid ethanol was removed, water was added, and the product was isolated with ether and chromatographed on silica gel. Elution with 4% ethyl acetate–benzene gave the monopropionate (14) as an oil (50 mg), $\nu_{max.}$ (film) 1 190s, 1 735s, and 3 460s cm^{-1}, τ 4.32 (2 H, m, =CH), 4.83br (1 H, s, C*H*·OCOEt), 5.83br (1 H, s, C*H*·OH), 7.64 (2 H, q, *J* 8 Hz, CO·C*H*$_2$Me), 8.26 (3 H, d, *J* 5 Hz, =CH*Me*), 8.83 (3 H, t, *J* 8 Hz, CH_2*Me*), and 9.08 (3 H, s, CMe).

Reaction of the allylic alcohol (14) (50 mg) with ethyl orthopropionate for 20 h gave the oily diesters (12) (46 mg), $\nu_{max.}$ 975w, 1 190m, and 1 735s cm^{-1}. This material was treated in a way similar to that described for the diesters (11) in order to convert the ethoxycarbonyl group into a methyl group. This procedure yielded the oily alcohol (19), which was characterised as the 3,5-dinitrobenzoate (22 mg), m.p. 139—140° (undepressed on admixture with authentic material), $[\alpha]_D^{25}$ +69.5°; the n.m.r. spectrum was identical with that of authentic material.

Conversion of the Diol (5) *into the Alcohol* (22).—To a stirred solution of the diol (5) (450 mg) in pyridine (7 cm^3) at 0 °C toluene-*p*-sulphonyl chloride (607 mg) was added; the mixture was then allowed to warm to 22 °C and stirring was continued for 21 h. Water (12 cm^3) was then added and stirring was continued for 15 min; the mixture was then poured into dilute hydrochloric acid and the product was isolated with ether. The monotosylate (6) formed an oil (747 mg), $\nu_{max.}$ (film) 945s, 1 173s, 1 188s, 1 355s, 1 600m, 3 400m, and 3 550m cm^{-1}, τ 7.55 (3 H, s, Ar*Me*), 9.03 (3 H, d, *J* 7 Hz, CH*Me*), and 9.11 (3 H, s, CMe). A portion (204 mg) was stirred with 2,3-dihydropyran (118 mg) and toluene-*p*-sulphonic acid (8 mg) in ether (5 cm^3) at 23 °C for 19 h. Evaporation under reduced pressure, and chromatography on neutral alumina (grade III; 4 g) (benzene) gave the tetrahydropyranyl ether (21) (262 mg) as an oil, homogeneous to t.l.c.

To a portion of the ether (21) (245 mg) in dry ether (2 cm^3) and dry tetrahydrofuran (2 cm^3) under nitrogen at −78 °C, a solution of dilithium tetrachlorocuprate in tetrahydrofuran (0.1M; 0.3 cm^3) was added, and the solution was stirred during the dropwise addition of a solution (3 cm^3) of the Grignard reagent prepared from 4-chloro-2-methylbut-1-ene (1.0 g) and magnesium (250 mg) in ether (4 cm^3) and tetrahydrofuran (4 cm^3). The mixture was allowed to warm to 20 °C during 1½ h, and stirring was continued for 15 h. It was then cooled to 0 °C, and 2N-hydrochloric acid (12 cm^3) was added dropwise, followed by saturated aqueous sodium chloride (20 cm^3) and ether (20 cm^3); the ether-soluble product (207 mg) was then isolated, and the tetrahydropyranyl ether group was removed by treatment with ethanolic N-hydrogen chloride (2 cm^3) at 22 °C for 20 min, with work-up in the usual way. Chromatography on

neutral alumina (benzene) gave the unsaturated alcohol (22) as an oil (109 mg), $\nu_{max.}$ (film) 883s, 1 648m, 3 070w, and 3 420m cm^{-1}, τ 5.33br (2 H, s, $W_{\frac{1}{2}}$ 4 Hz, $=CH_2$), 5.95br (1 H, s, $W_{\frac{1}{2}}$ 7 Hz, CH·O), 8.29 (3 H, s, $-CMe=CH_2$), 9.07 (3 H, s, CMe), and 9.10 (3 H, d, J 6 Hz, CH*Me*). The 3,5-*dinitrobenzoate* of 1β-[(R)-1,5-*dimethylhex*-5-*enyl*]-4β-*hydroxy*-7aβ-*methyl*-3aα,4,5,6,7,7aβ-*hexahydroindane* separated from chloroform–light petroleum as needles, m.p. 141—144°, $[\alpha]_D^{21}$ +62.9° (Found: C, 65.6; H, 7.3; N, 6.25. $C_{25}H_{34}N_2O_6$ requires C, 65.5; H, 7.45; N, 6.1%).

A portion of the alcohol (22) was hydrogenated over palladium in ethanol, and the product was isolated as the 3,5-dinitrobenzoate, which formed needles (from chloroform–light petroleum), m.p. 163—165° (lit.,[8] 164°).

The Diol (23).—The unsaturated alcohol (22) (223 mg) in tetrahydrofuran (5 cm^3) was added to a stirred mixture of mercury(II) acetate (288 mg) in water (2.5 cm^3) and tetrahydrofuran (2.5 cm^3), and the mixture was stirred at 20 °C for 2 h. 3N-Sodium hydroxide (4 cm^3) was then added, followed by 0.5M-sodium borohydride (4 cm^3) in 3N-sodium hydroxide. Following the addition of saturated aqueous sodium chloride (15 cm^3) the product was isolated with ether and chromatographed on neutral alumina (grade III; 20 g). Elution with benzene gave the alcohol (22) (60 mg); further elution with 20% ethyl acetate–benzene gave the diol (23). The 4β-*hydroxy*-1β-[(R)-5-*hydroxy*-1,5-*dimethylhexyl*]-7aβ-*methyl*-3aα,4,5,6,7,7aβ-*hexahydroindane* separated from ether–light petroleum as needles (155 mg), m.p. 91—92°, $[\alpha]_D^{21}$ +44.2°, $\nu_{max.}$ (Nujol) 3 350s cm^{-1}, τ 5.94 (1 H, s, $W_{\frac{1}{2}}$ 7 Hz, CH·O), 8.69 (6 H, s, $O{\cdot}CMe_2$), 9.06 (3 H, s, CMe), and 9.09 (3 H, d, J 6 Hz, CH*Me*) (Found: C, 77.0; H, 12.2. $C_{18}H_{34}O_2$ requires C, 76.55; H, 12.15%).

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[8] H. H. Inhoffen, G. Quinkert, S. Schütz, D. Kampe, and G. F. Domagk, *Chem. Ber.*, 1957, **90**, 664.