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SESQUITERPENOIDS—VI

THE CHEMISTRY OF SOME COMPOUNDS IN THE 14-NOREUDESMANE SERIES

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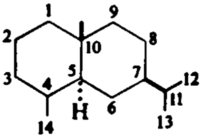
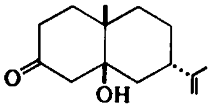
Abstract—The preparation of some compounds in the 14-noreudesmane series is reported. The equilibrium between (+)-7β(H)-14-noreudesm-4-en-3,6-dione (XIII; R = H) and (+)-14-noreudesm-4-en-3,6-dione (XIV; R = H) is discussed. The synthesis of (+)-5β,7β(H)-14-noreudesm-4-one (XVI) whose absolute configuration is enantiomeric to that of D-valeranone (XVII) is described.

PREVIOUS papers in this series have been concerned with the chemistry of some 7β(H)-eudesmanes.[1] (The nomenclature is as before based upon the eudesmane (I).) In this paper these investigations are extended to the 14-nor-series, the focus of attention being the equilibrium between the ketones XIII (R = H) and XIV (R = H).

The ketol II with the absolute configuration shown was prepared by the reaction of 1-chlorobutan-3-one with the enolate of (−)-dihydrocarvone in tetrahydrofuran. The evidence for the absolute configuration of this ketol rests upon the following points of comparison with the ketol III of known absolute configuration.[2] The RD curve of II, a^{301}_{265} +25(MeOH), is similar to that of the ketol III, a^{304}_{264} +27(MeOH)*. On dehydration with ethanolic hydrochloric acid the ketone IV was obtained whose RD curve, a^{358}_{310} +24·5(MeOH), is similar to that of the ketone V, a^{350}_{312} +28.[3] The 7α-orientation of the isopropylidene side-chain was confirmed by treating the ketone IV with conc sulphuric acid, when the dienone VI was formed. This isomerization was shown by McQuillin[2] to occur in the cyperone series only when the side-chain has an α-orientation. These results then allow the absolute configuration of the ketol II to be written as shown.



I



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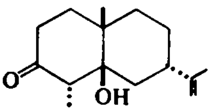

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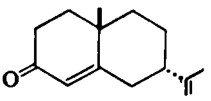
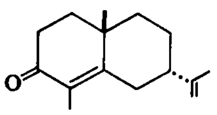
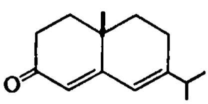


IV



V



VI

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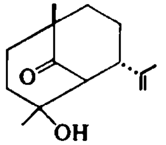
* $a^{\lambda_1}_{\lambda_2}$ is defined as the difference between the molecular rotation ϕ_{λ_1} at the extremum of longer wavelength minus the molecular rotation ϕ_{λ_2} at the extremum of shorter wavelength divided by 100.

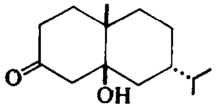
[1] Part IV, *Tetrahedron* **21**, 791 (1965); Part V, *Tetrahedron Letters* 969 (1966).

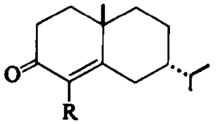
[2] F. J. McQuillin, *J. Chem. Soc.* 528 (1955); R. Howe and F. J. McQuillin, *Ibid.* 2423 (1955), 2670 (1956).

[3] Cf. C. Djerassi, R. Riniker and B. Riniker, *J. Amer. Chem. Soc.* **78**, 6377 (1956).

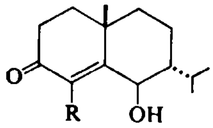
One point of interest remains in connection with the ketol II. It has been shown[4] that some ketols produced in the annelation reaction have an alternative bridged ring structure, so that if the ketol II were analogous, it would have the structure VII. However the NMR spectrum of this ketol clearly excludes this possibility since only two methyl singlets were apparent (at 8·82 $\tau(C_{10}\text{–}CH_3)$ and 8·32 $\tau(\text{—}\underset{\underset{CH_2}{\|}}{C}\text{—}CH_3)$).

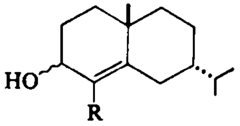

VII

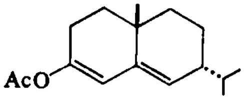

VIII


IX

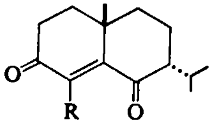
The ketol II took up 1 mole of hydrogen to give the corresponding saturated ketol VIII which was dehydrated with ethanolic hydrochloric acid to the ketone IX (R = H). This ketone did not yield the hydroxy-ketone X (R = H) by reaction with oxygen in the presence of sodium isopropoxide, unlike its analogue IX (R = Me) which readily afforded the hydroxy-ketone X (R = Me) under the same conditions.[2] The only material isolated from the reaction was the hydroxy-compound XI (R = H) arising from direct reduction of the ketone IX (R = H) by isopropoxide ion. The reason for this difference is not at all clear, considering that the RD measurements indicate close similarity in conformation between the two series of compounds. However X (R = H) was obtained by another route. The enol-acetate XII from the ketone IX (R = H) was treated with one mole of perbenzoic acid and the product saponified with potassium hydroxide in ethanol. The hydroxy-ketone X (R = H) was thereby obtained as a gum, characterized by its yielding the 2,4-dinitrophenylhydrazone of the dienone VI.

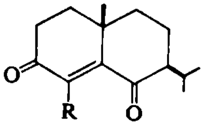

X


XI


XII

Oxidation of the hydroxy-ketone X (R = H) with 8N chromic acid in acetone gave the crystalline diketone XIII (R = H) which isomerized to the 7α(H)-epimer XIV (R = H) in cold ethanolic potassium hydroxide solution. An investigation of this reaction revealed, not unexpectedly, an equilibrium between these two diketones such that at 25° the equilibrium mixture contained 76 ± 2% of the diketone XIV


XIII


XIV

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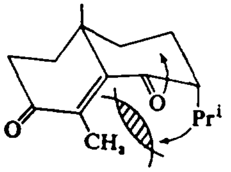
[4] W. S. Johnson, J. J. Korst, R. A. Clement and J. Dutta, *J. Amer. Chem. Soc.* **82**, 614 (1960); J. A. Marshall and W. I. Fanta, *J. Org. Chem.* **29**, 2501 (1964).

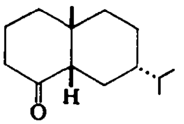
(R = H). This corresponds to $\Delta G_{298} \approx -0{\cdot}7$ kcals/mole as a mean value for the free-energy change in the reaction XIII (R = H) → XIV (R = H). The composition of the equilibrium mixture was determined by comparing the optical rotations of the mixture and the pure components, and by direct chromatographic separation.

Some interest attaches to a comparison of this free-energy change with that previously found, $-1{\cdot}1$ kcals/mole, for the reaction XIII (R = Me) → XIV (R = Me).[5] In the previous paper[5] an explanation was suggested for the high value of this free-energy change compared to the usual value of somewhat less than 1 kcal/mole for the change $Pr^{i}_{ax} \rightarrow Pr^{i}_{eq}$ in 2-isopropylcyclohexanones. (There is no generally agreed value for this free energy change, though Allinger and Blatter[6] in a study of the equilibrium between *cis*- and *trans*-2-isopropyl-4-t-butylcyclohexanone, and Rickborn[7] in a similar study upon *cis*- and *trans*-1,2-diisopropylcyclohexanone, and more recently Djerassi *et al.*[8] in a study of some steroid examples conclude that it is probably in the region of 0·6 kcals/mole.) The high value for the free-energy change in the reaction XIII (R = Me) → XIV (R = Me) was explained by suggesting that interaction between the $C_{(4)}$–CH_3 and the $C_{(6)}{=}O$ was relieved somewhat by a twisting of ring B in the sense shown in XV, thereby increasing the non-bonded interactions suffered by the isopropyl group. In the reaction XIII (R = H) → XIV (R = H) of course, such an effect is absent, and the free-energy change associated with the isomerization is approximately that for the epimerization $Pr^{i}_{ax} \rightarrow Pr^{i}_{eq}$ in 2-isopropylcyclohexanones.

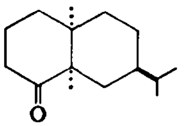


XV

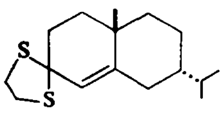
The ketone IX (R = H) was the starting point for a synthesis of the *cis*-decalone (XVI), whose stereochemistry is enantiomeric to that of natural D-valeranone (XVII).[9,10] The ketone IX (R = H) was converted into its ethylenethioketal (XVIII) which was smoothly desulphurized by W2 Raney nickel to the olefin XIX. This on hydroboration and oxidation of the organoborane in the usual way gave a single



XVI



XVII



XVIII

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[5] D. W. Theobald, *Tetrahedron* **20**, 1455 (1964).

[6] N. L. Allinger and H. M. Blatter, *J. Amer. Chem. Soc.* **83**, 994 (1961).

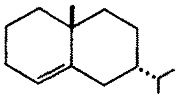
[7] B. Rickborn, *J. Amer. Chem. Soc.* **84**, 2414 (1962).

[8] C. Djerassi, P. A. Hart and C. Beard, *J. Amer. Chem. Soc.* **86**, 85 (1964).

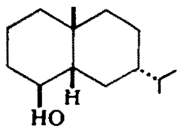
[9] W. Klyne, S. C. Bhattacharyya, S. K. Paknikar, C. S. Narayanan, K. S. Kulkani, J. Krěpinský, M. Romaňuk, V. Herout and F. Šorm, *Tetrahedron Letters* 1443 (1964) and references there cited.

[10] A preliminary report of this work appeared in *Tetrahedron Letters* 969 (1966); cf. J. A. Marshall, W. I. Fanta and G. L. Bundy, *Ibid.* 4807 (1965).

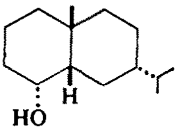
crystalline alcohol (XX). The evidence for the stereochemistry of XX is as follows. Oxidation with 8N chromic acid in acetone gave the ketone XVI, which was recovered unchanged from a refluxing solution of sodium ethoxide in ethanol, and from the protonation of its enolate anion formed with sodium hydride in boiling tetrahydrofuran. Reduction of this ketone with sodium in ethanol gave a new alcohol XXI, suggesting since the ring-fusion is stable to sodium ethoxide, that in the alcohol XX the hydroxyl group has the less stable axial orientation. Given the usual mechanism of hydroboration, this is only possible if the alcohol XX has a *cis* ring-fusion, and moreover exists in the non-steroid conformation. It is evident that the preference for an equatorial as opposed to an axial isopropyl group which is met by the non-steroid conformation, dictates the stereochemical course of the hydroboration, and this influence is again in evidence in the hydroboration of the alcohol XI (R = Me). Oxidation of the product derived from this alcohol gave the ketol XXII in high yield, and this ketol is known to possess a non-steroid conformation.[2,11] The stereochemistry of the alcohol XX and that of the ketone XVI follow from these results.



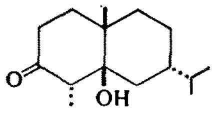
XIX



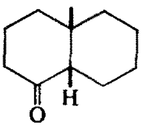
XX



XXI



XXII



XXIII

Two points of interest attach to the ketone XVI. First, its stability to epimerizing conditions merits comment. Undoubtedly this must be attributed to a preference for an equatorial isopropyl group which can only be realised with a *cis* ring-fusion in the non-steroid conformation. (There is still some disagreement in the literature about the importance of non-steroid conformations in *cis*-decalones.[12]) The free-energy change for $\mathrm{Pr}^{i}_{ax} \rightarrow \mathrm{Pr}^{i}_{eq}$ in cyclohexanes is generally agreed to be 2·0–2·5 kcals/mole[13], whereas that for the conversion of the *cis*-decalone (XXIII) to its *trans*-isomer is almost zero.[14] Given these figures, it is not surprising that the *cis*-decalone (XVI) shows no tendency to epimerize.

The second point of interest about this decalone concerns its RD curve, a^{815}_{271} +110, compared to that of natural D-valeranone (XVII), a^{323}_{273} −116. This indicates that the stereochemistry of XVI is enantiomeric to that of XVII, and therefore confirms the absolute configuration of D-valeranone as XVII.[9]

[11] T. G. Halsall, D. W. Theobald and K. B. Walshaw, *J. Chem. Soc.* 1029 (1964).

[12] K. L. Williamson and T. A. Spencer, *Tetrahedron Letters* 3267 (1965); C. Djerassi, J. Burakevich, J. W. Chamberlain, D. Elad, T. Toda and G. Stork, *J. Amer. Chem. Soc.* **86**, 465 (1964).

[13] E. L. Eliel and T. J. Brett, *J. Amer. Chem. Soc.* **87**, 5039 (1965); B. J. Armitage, G. W. Kenner and M. J. T. Robinson, *Tetrahedron* **20**, 747 (1964); N. L. Allinger and S. Hu, *J. Org. Chem.* **27**, 3417 (1962); N. L. Allinger and F. A. Freiberg, *Ibid.* **31**, 894 (1966).

[14] F. Sondheimer and D. Rosenthal, *J. Amer. Chem. Soc.* **80**, 3995 (1958).

EXPERIMENTAL

M.ps are uncorrected. Specific rotations—chf solns at 20°. UV spectra—EtOH solns, Unicam SP 700. IR spectra—Perkin-Elmer spectrophotometers PE-21 and Infracord 137 with NaCl prisms. RD measurements—Professor W. Klyne, Westfield College, University of London. NMR spectra—PE-R 10 instrument at 60 Mc/s.

Al_2O_3 for chromatography—Peter Spence's Grade H, deactivated with 5% of 10% AcOH. Petroleum ether—b.p. 60–80°, unless otherwise stated.

(−)-*5β-Hydroxy-7β*(H)-14-*noreudesm*-11-*en*-3-*one* (II). (−)-Dihydrocarvone (20·8 g) was added to a suspension of NaH (3·5 g) in THF (100 ml) under N. A few drops EtOH were added to start the reaction, which was completed by heating under reflux for 2 hr. 1-Chlorobutan-3-one (14·2 g) was added at 25° and the mixture stirred for 1 hr. Excess dil aqueous AcOH was added at 0° and the product isolated in ether. Distillation gave the following fractions (i) b.p. 60–80°/0·5 mm (8 g), largely (−)-dihydrocarvone, (ii) b.p. 80–105°/0·5 mm (10 g), an oil which partly crystallized on standing, and (iii) b.p. 146–148°/0·5 mm (10 g), which almost completely crystallized. Recrystallization of fractions (ii) and (iii) from pet. ether gave (−)-*5β-hydroxy-7β*-(H)-14-*noreudesm*-11-*en*-3-*one* (II) as prisms (13 g), m.p. 110–1°; $[\alpha]_D$ −58° (*c*, 2·6). IR (Nujol): 3600, 1710, 1650, 893 cm^{-1}. UV (EtOH) 295 mμ (ε = 70). NMR ($CCl_4/SiMe_4$): 8·32, 8·82 τ. ORD (in MeOH): a_{265}^{301} +25. (Found: C, 75·7; H, 9·8. $C_{14}H_{22}O_2$ requires: C, 75·7; H, 9·9%.)

(+)-7β(H)-14-*Noreudesma*-4,11-*dien*-3-*one* (IV). A soln of II (1·0 g) in EtOH (15 ml) containing conc HCl (1·8 ml) was kept at 0° for 7 days. Neutralization with $NaHCO_3$, dilution with water and extraction with ether gave an oil which was adsorbed on alumina (50 g). Elution with pet. ether-benzene (1:1) gave (+)-7β(H)-14-*noreudesma*-4,11-*dien*-3-*one* (IV) as an oil (800 mg), b.p. 98–101°/0·1 mm; $[\alpha]_D$ +185° (*c*, 1·3); n_D^{19} 1·5353. IR (film): 1665, 1610, 893 cm^{-1}. UV (EtOH): 241 mμ (ε = 16200). ORD (MeOH): a_{310}^{353} +24·5. (Found: C, 82·1; H, 9·6. $C_{14}H_{20}O$ requires: C, 82·4; H, 9·8%.)

The 2,4-*dinitrophenylhydrazone* crystallized from EtOH as scarlet needles, m.p. 139–140°. (Found: C, 62·8; H, 6·6; N, 14·6. $C_{20}H_{24}N_4O_4$ requires: C, 62·5; H, 6·3; N, 14·6%.)

(+)-14-*Noreudesma*-4,6-*dien*-3-*one* (VI). A soln of IV (1·0 g) in H_2SO_4 (50% v/v; 15 ml) was kept at 10° for 6 hr. Dilution with water and extraction with ether gave an oil which was filtered through alumina (50 g) in benzene. (+)-14-*Noreudesma*-4,6-*dien*-3-*one* (VI) was obtained as an oil (780 mg), b.p. 100–105°/0·2 mm; $[\alpha]_D$ +608° (*c*, 0·7); n_D^{20} 1·5622. IR (film): 1670, 1645, 1605, 1375, 1355, 1275, 1250, 1225 cm^{-1}. UV (EtOH): 295 mμ (ε = 24600). (Found: C, 82·0; H, 9·6. $C_{14}H_{20}O$ requires: C, 82·4; H, 9·8%.)

The 2,4-*dinitrophenylhydrazone* crystallized from EtOH as crimson plates, m.p. 183–184°. (Found: C, 62·7; H, 6·2; N, 14·5. $C_{20}H_{24}N_4O_4$ requires: C, 62·5; H, 6·3; N, 14·6%.)

The *semicarbazone* crystallized from EtOH aq as needles, m.p. 240–242°. (Found: C, 68·9; H, 8·5; N, 16·1. $C_{15}H_{23}N_3O$ requires: C, 69·0; H, 8·8; N, 16·1%.)

(−)-*5β-Hydroxy-7β*(H)-14-*noreudesman*-3-*one* (VIII). The ketol II took up 1 mole H_2 on Pt in EtOH to give (−)-*5β-hydroxy-7β*(H)-14-*noreudesman*-3-*one* (VIII) which crystallized from pet. ether at 0° as prisms, m.p. 61–62°; $[\alpha]_D$ −64° (*c*, 2·9). IR (Nujol and HCB): 3550, 1710, 1380, 1365 cm^{-1}. (Found: C, 75·1; H, 10·4. $C_{14}H_{24}O_2$ requires: C, 75·0; H, 10·7%.)

(+)-7β(H)-14-*Noreudesm*-4-*en*-3-*one* (IX; R = H). A soln of VIII (1·0 g) in EtOH (10 ml) containing conc HCl (1·5 ml) was kept at 0° for 7 days. The mixture was neutralized with $NaHCO_3$ and diluted with water. Extraction with ether gave an oil which was filtered in pet. ether–benzene (1:1) through alumina (60 g). This afforded IX (R = H) as an oil (850 mg), b.p. 100–104°/0·2 mm; [α] +170° (*c*, 1·1); n_D^{20} 1·5205. IR (film): 1660, 1640, 865 cm^{-1}. UV (EtOH): 240 mμ (ε = 15400). Lit. records: [12]$[\alpha]_D$ +65° (*c*, 1·44).

The 2,4-dinitrophenylhydrazone crystallized from EtOH as scarlet needles, m.p. 160–161°. Lit. records:[12] m.p. 195–197°.

The *semicarbazone* crustallized from EtOH aq as prisms, m.p. 264–265°. (Found: C, 68·2; H, 9·2; N, 15·8. $C_{15}H_{25}N_3O$ requires: C, 68·4; H, 9·5; N, 16·0%.)

(+)-3-*Acetoxy-7β*(H)-14-*noreudesma*-3,5-*diene* (XII). A soln of IX (R = H; 1·0 g) in isopropenyl acetate (40 ml) containing toluene-*p*-sulphonic acid (160 mg) was heated under reflux for 8 hr. Solid $NaHCO_3$ was added to the cooled soln, and the product isolated in ether. Removal of the solvents left a pale yellow oil (900 mg) which was absorbed on alumina (40 g).

Elution with pet. ether gave (+)-3-*acetoxy-7β*(H)-14-*noreudesma*-3,5-*diene* (XII) as an oil (390 mg), b.p. 108–110°/0·1 mm; $[\alpha]_D$ +78° (*c*, 3·0); n_D^{19} 1·5100. IR (film): 1755, 1720, 1670, 1220, 1080 cm^{-1}. UV (EtOH): 235 mμ ($\varepsilon = 17200$). (Found: C, 77·3; H, 9·4. $C_{16}H_{24}O_2$ requires: C, 77·4; H, 9·7%.)

(+)-6ξ-*Hydroxy-7β*(H)-14-*noreudesm*-4-*en*-3-*one* (X; R = H). The enol-acetate XII (500 mg) in ether (15 ml) was treated with a soln of perbenzoic acid (165 mg) in ether (10 ml) and the mixture set aside in the dark for 60 hr at 20°. The ether was removed, the residue dissolved in EtOH (15 ml), KOH (0·6 g) added, and the mixture kept at 50° under N for 3 hr. The product was isolated in ether as a gum (450 mg) which was adsorbed on alumina (30 g).

Elution with pet. ether–benzene (1:1) gave IX (R = H) as an oil (60 mg).

Elution with benzene–ether (19:1) gave (+)-6ξ-*hydroxy-7β*(H)-14-*noreudesm*-4-*en*-3-*one* (X; R = H) as a gum (290 mg), $[\alpha]_D$ +31° (*c*, 2·1). IR (Nujol); 3340, 1675, 1610, 850 cm^{-1}. UV (EtOH): 241 mμ ($\varepsilon = 12{,}300$). No entirely satisfactory analysis figures were obtained for this compound, which was never obtained crystalline. However it was characterized by the preparation from it of the 2,4-dinitrophenylhydrazone of VI as crimson plates, m.p. 182–184°.

Further elution of the column gave only small quantities of non-crystalline materials which were not characterized.

(+)-7β(H)-14-*Noreudesm*-4-*en*-3,6-*dione* (XIII; R = H). The hydroxy-ketone X (R = H; 400 mg) in acetone (10 ml) was treated with 8N chromic acid at 0° until an orange colour persisted. The product was recovered in ether. (+)-7β-(H)14-*Noreudesm*-4-*en*-3,6-*dione* (XIII; R = H) crystallized from pet. ether at 0° as needles (340 mg), m.p. 84–85°; $[\alpha]_D$ +256° (*c*, 0·7). IR (Nujol and HCB): 1660, 1380, 1360 cm^{-1}. UV (EtOH): 294 mμ ($\varepsilon = 12100$). (Found: C, 76·4; H, 9·0. $C_{14}H_{20}O_2$ requires: C, 76·4; H, 9·1%.)

The 2,4-*dinitrophenylhydrazone* crystallized from EtOH as scarlet needles, m.p. 210–211°. (Found: C, 59·7; H, 6·0; N, 13·8. $C_{20}H_{24}N_4O_5$ requires: C, 60·0; H, 6·0; N, 14·0%.)

(+)-14-*Noreudesm*-4-*en*-3,6-*dione* (XIV; R = H). A soln of XIII (R = H; 1·0 g) and KOH (3·0 g) in EtOH (30 ml) and water (5 ml) was kept under N at 25° for 48 hr. Dilution with water and extraction with ether gave an oil (950 mg). Thus was absorbed on alumina (130 g). Elution with pet. ether–benzene (5:3) gave (+)-14-*noreudesm*-4-*en*-3,6-*dione* (XIV; R = H) which crystallized from pet. ether at −60° as prisms (740 mg), m.p. 38–39°; $[\alpha]_D$ +106° (*c*, 1·1). IR (Nujol and HCB): 1670, 1380, 1360 cm^{-1}. UV (EtOH): 250 mμ ($\varepsilon = 13{,}000$). (Found: C, 76·1; H, 9·0. $C_{14}H_{20}O_2$ requires: C, 76·4; H, 9·1%.)

The 2,4-*dinitrophenylhydrazone* crystallized from EtOH as red needles, m.p. 188–189°. (Found: C, 60·0; H, 5·7; N, 13·6. $C_{20}H_{24}N_4O_5$ requires: C, 60·0; H, 6·0; N, 14·0%.)

Elution with pet. ether–benzene (10:7) gave XIII (R = H) which crystallized from pet. ether at 0° as prisms (210 mg), m.p. 84–85°.

Several estimations of the composition of the equilibrium mixture in EtOH containing catalytic quantities of KOH (2% by wt of the ketone) at 25° by rotation measurements and chromatography gave a figure of 76 ± 2% for the amount of XIV (R = H) present at equilibrium.

The ethylenethioketal (XVIII). The ketone IX (R = H; 230 mg) in AcOH (1 ml) was treated with ethanedithiol (0·3 ml) and BF_3 etherate (0·3 ml). After 30 min at 20°, the mixture was diluted with water and neutralized with $NaHCO_3$. Extraction with ether gave a solid which was filtered through alumina (10 g) in pet. ether. The *ethylenethioketal* (XVIII) crystallized from MeOH as needles (220 mg), m.p. 130–131°; $[\alpha]_D$ +121° (*c*, 1·4). IR (Nujol): 1640, 855 cm^{-1}. NMR ($CCl_4/SiMe_4$): 4·6 τ ($\underset{\substack{|\\ \mathrm{H}}}{—\mathrm{C}}{=}\mathrm{C}\!<$). (Found: C, 68·4; H, 9·3; S, 22·8. $C_{16}H_{26}S_2$ requires: C, 68.1; H, 9·2; S, 22·7%.)

(+)-7β(H)-14-*Noreudesm*-4-*ene* (XIX). The thioketal XVIII (1·0 g) was stirred with excess W2 Raney Ni[15] in EtOH (30 ml) at 20° for 1 hr. Filtration and removal of the solvent gave an oil which was filtered through alumina (30 g) in pet. ether. (+)-7β(H)-14-*Noreudesm*-4-*ene* was obtained as an oil (500 mg), b.p. 55–60°/0·4; $[\alpha]_D$ +52° (*c*, 2·5); n_D^{20} 1·4910. IR (film): 1645, 1380, 1360, 1015, 995, 810, 800 cm^{-1}. (Found: C, 87·2; H, 12·4. $C_{14}H_{24}$ requires: C, 87·5; H, 12·5%.)

(−)-4β-*Hydroxy*-5β,7β(H)-14-*noreudesmane* (XX). Excess diborane in N (generated from the reaction of BF_3–Et_2O and LAH in ether) was passed into a solution of XIX (500 mg) in ether (40 ml) at 0°. The mixture was allowed to stand for 1 hr at 20°, and the solvent and excess diborane removed *in vacuo*. A solution of the glassy organoborane in EtOH (15 ml) and water (5 ml) containing KOH

[15] R. Mozingo, *Org. Synth. Coll. Vol.* 3, 181.

(2 g) was treated with H_2O_2 (5 ml of 30%), and the mixture stirred for 1 hr at 20°. The product, which was recovered in ether, crystallized from pet. ether to give (−)-4β-*hydroxy*-5β,7β(H)-14-*noreudesmane* (XX) as prisms (410 mg), m.p. 87–88°; $[\alpha]_D$ −31° (*c*, 3·3). (Found: C, 79·9; H, 12·4. $C_{14}H_{26}O$ requires: C, 80·0; H, 12·4%).

(+)-5β,7β(H)-14-*Noreudesman-4-one* (XVI). The alcohol XX; (250 mg) in acetone (10 ml) was treated with 8N chromic acid at 0° until an orange colour persisted. The product was recovered in the usual way by dilution with water and extraction with ether, and was obtained as an oil. This was filtered in pet. ether–benzene (10:1) through alumina (20 g) to give (+)-5β,7β(H)-14-*noreudesman-4-one* (XVI) as an oil (200 mg), b.p. 95–98°/0·1 mm; $[\alpha]_D$ +76° (*c*, 3·8); n_D^{20} 1·4887. IR (film): 1710, 1380, 1360, 1230, 1155, 965 cm⁻¹. ORD (hexane) a_{273}^{327} +108; (MeOH) a_{271}^{315} +110. (Found: C, 80·5; H, 11·2. $C_{14}H_{24}O$ requires: C, 80·8; H, 11·5%.)

The 2,4-*dinitrophenylhydrazone* crystallized from EtOH as orange plates, m.p. 172–173°. (Found: C, 61·8; H, 7·2; N, 14·1. $C_{20}H_{28}N_4O_4$ requires: C, 61.9; H, 7·2; N, 14·4%.)

The *semicarbazone* crystallized from EtOHaq. as prisms, m.p. 168–170°. (Found: C, 67·6; H, 10·1; N, 15·5. $C_{15}H_{27}N_3O$ requires: C, 67·9; H, 10·2; N, 15·9%.)

The ketone XVI was recovered from a refluxing solution of EtONa in EtOH, and was also obtained when a soln of its enol anion (made with NaH) in THF was acidified with AcOH.

(−)-4α-*Hydroxy*-5β,7β(H)-14-*noreudesmane* (XXI). Na (1·0 g) was added in small pieces to a soln of XVI (300 mg) in EtOH (20 ml) under N. When the Na was dissolved, the soln diluted with water and the product recovered in ether. (−)-4α-*Hydroxy*-5β,7β(H)-14-*noreudesmane* (XXI) was obtained as a solid which crystallized from pet. ether as needles (210 mg), m.p. 91–92°; $[\alpha]_D$ −8° (*c*, 5·1). (Found: C, 79·8; H, 12·3. $C_{14}H_{26}O$ requires: C, 80.0; H, 12·4%.)

(+)-3ξ-*Hydroxy*-7β(H)-*eudesm-4-ene* (XI; R = Me). The ketone IX (R = Me) was reduced with excess LAH in ether at 20°. (+)-3ξ-*Hydroxy*-7β(H)-*eudesm-4-ene* (XI; R = Me) crystallized from pet. ether at −60° as prisms, m.p. 84–85°; $[\alpha]_D$ +19° (*c*, 2·1). (Found: C, 81·1; H, 11·6. $C_{15}H_{26}O$ requires: C, 81·1; H, 11·7%.)

The hydroboration of the alcohol (XI; R = Me). Excess diborane in N was passed into a soln of XI (R = Me; 500 mg) in ether (20 ml) at 0°. The mixture was then allowed to stand 1 hr at 20°. The ether and excess diborane were then removed *in vacuo*, and the organoborane dissolved in EtOH (15 ml) and water (7 ml) containing KOH (2 g) and H_2O_2 (8 ml of 30%). This mixture was stirred 1 hr at 20°. The product was recovered as a viscous oil (460 mg) by extraction with ether. It was oxidized with 8N chromic acid in acetone at 0° to give XXII which crystallized from pet. ether as prisms (390 mg), m.p. 64–65°; $[\alpha]_D$ −49° (*c*, 3·5). Lit. records:[6] m.p. 64–66°; $[\alpha]_D$ −52° (*c*, 1·6).

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