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SESQUITERPENOIDS—I

THE CHEMISTRY OF SOME 7β(H)-EUDESM-11-EN-3,6-DIONES AND RELATED COMPOUNDS

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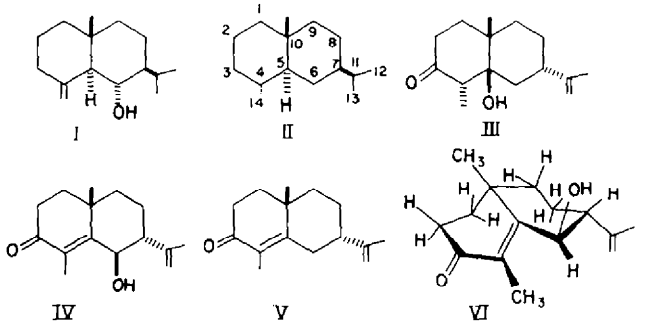
Abstract—The chemistry of some derivatives of (+)-6β-hydroxy-7β(H)-eudesma-4,11-dien-3-one (IV) is described. In particular, the stereochemistry of the reduction products of (+)-7β(H)-eudesma-4,11-dien-3-6-dione (IX) with zinc in acetic acid is established. The 6β-configuration for the hydroxyl group in the ketone (IV) is confirmed by a chemical method.

THE results disclosed in this paper from part of a set of investigations into the synthesis of sesquiterpenes of the eudesmane group,[1] in particular those such as junenol (I)[2] in particular those such as junenol (I)[2] which bear an oxygen function at position 6. Eudesmane itself has the absolute stereochemistry (II) upon which the nomenclature used in this paper is based. The progress of the synthetic work will be reported shortly. Meanwhile a recent publication[3] describing 3,6-diones in both the 5α- and the 5β-cholestane series makes this an opportune moment to divulge some results obtained with similar compounds in the 7β(H)-eudesmane series.

A convenient point of departure for these investigations was (−)-5β-hydroxy-4β,(H)-eudesm-11-en-3-one (III),which was prepared by a modification[4] of the procedure described by McQuillin.[5] This compound was easily converted by oxygen in the



[1] W. Cocker and T. B. H. McMurry, *Tetrahedron* **8**, 181 (1960).
[2] V. Herout, O. Motl and F. Sorm, *Coll. Czech. Chem. Comm.* **22**, 785 (1957); A. M. Shaligram, A. S. Rao and S. C. Bhattacharyya, *Chem. & Ind.* 469 (1960); *Tetrahedron* **18**, 969 (1962).
[3] S. Julia, B. Decouvelaere, J-P. Lavaux, C. Moutonnier and P. Simon, *Bull. Soc. Chim. Fr.* 1223 (1963).
[4] T. G. Halsall, D. W. Theobald and K. B. Walshaw, *J. Chem. Soc.*, in press.
[5] F. J. McQuillin, *J. Chem. Soc.* 528 (1955); R. Howe and F. J. McQuillin, *Ibid.* 2423 (1955), 2670 (1956).

presence of sodium isopropoxide to (+)-6β-hydroxy-7β(H)-eudesma-4,11-dien-3-one (IV).[6] A 6β-configuration was given to the hydroxyl group in this compound by Howe and McQuillin[6] for the following reasons—(i) the resistance to isomerisation to the corresponding 3,6-dione thus indicating a stable orientation for the 6-hydroxyl group, (ii) the fact that in a boat form for ring B, such as is thought to occur in (+)-7β(H)-eudesma-4,11-dien-3-one (V), a 6β-substituent would occasion less steric interaction than a 6α-, and (iii) the evidence of molecular rotations and UV absorption spectra. The results described here strongly support a 6β-configuration for the hydroxyl group.

The optical rotatory dispersion curve of (+)-7β(H)-eudesma-4,11-dien-3-one (V) was shown some time ago to be quite unlike that of its 7α(H)-epimer, and rather like that of 8α-steroids in which either ring B or ring C must exist in a boat rather than a chair form.[7] The dispersion curve for the ketone (IV) was very similar to that of the ketone (V) except that the extremum at the shorter wavelength could not be measured ($a = +71{\cdot}8!$).* The conclusion must be then that both the ketones (IV) and (V) have ring B as a partial or complete boat. This achieves some relief from the steric compression which the molecules would suffer if ring B were a chair, and so carried an axial isopropenyl (in V) or an axial isopropenyl group and an axial hydroxyl group (in IV).

The principal peaks in the NMR spectrum of the ketone (IV) were remarkably free from multiplicity due to spin-spin coupling. This spectrum was measured in view of a recent publication[8] in which homoallylic spin-spin coupling was detected in similar compounds of the 7α(H)-series, between the proton at $C_{(6)}$ and the protons of the methyl group at $C_{(4)}$. In the cases examined, it appeared that the signal from the protons of the $C_{(4)}$-methyl group was a doublet when the proton at $C_{(6)}$ had the β-configuration, but a singlet when it had the α-configuration. The signal of the proton at $C_{(6)}$ appeared in all cases as a doublet due to strong coupling with the proton at $C_{(7)}$, but showed additional fine structure when the proton at $C_{(6)}$ had the β-configuration. The homoallylic coupling seemed to be strongest when the $C_{(6)}$—H bond was perpendicular to the plane defined by the system CH_3—$C_{(4)}$=$C_{(5)}$—$C_{(6)}$. In the spectrum obtained for the ketone (IV) the signal attributed to the $C_{(4)}$-methyl group (τ 8·17) was a singlet, and that attributed to the proton at $C_{(6)}$ (τ 5·56) showed negligible spin-spin splitting ($J < 1$ c/s). Spin-spin coupling between the $C_{(4)}$-methyl group and the proton at $C_{(6)}$, and between this proton and that at $C_{(7)}$ thus appeared minimal. Models show that these results are best accommodated by the conformation (VI), in which the $C_{(6)}$—H bond lies in the plane defined by CH_3—$C_{(4)}$=$C_{(5)}$—$C_{(6)}$ and in which the orthogonal projection of the angle between the $C_{(6)}$—H and the

* a is defined as the difference between the molecular rotation, $[\phi]_L$, at the extremum of longer wavelength *minus* thermomolecular rotation, $[\phi]_S$, at the extremum of shorter wavelength divided by 100. ! means that $[\phi]_S$ could not be measured, and so the value of a is a minimum value.

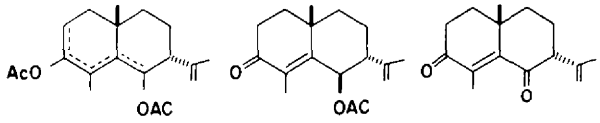
[6] H. M. E. Cardwell and F. J. McQuillin, *J. Chem. Soc.* 525 (1955); R. Howe and F. J. McQuillin, *Ibid.* 1513 (1958).

[7] C. Djerassi, R. Riniker and B. Riniker, *J. Amer. Chem. Soc.* **78**, 6377 (1956); C. Djerassi, H. Bendas and A. Segaloff, *J. Org. Chem.* **21**, 1056 (1956) C. Djerassi, A. J. Manson and A. Segaloff, *Ibid.* **21**, 490 (1956).

[8] J. T. Pinhey and S. Sternhell, *Tetrahedron Letters* No. 4, 275 (1963); D. J. Collins, J. J. Hobbs and S. Sternhell, *Ibid.* 197.

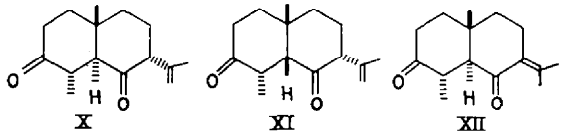
$C_{(7)}$—H bond is approximately 100°.[9] In such a conformation the steric interactions of the hydroxyl and isopropenyl groups are minimized.

The synthetic work which prompted these investigations, required the reduction of the Δ^4-double bond, and this was eventually accomplished in two ways. The hydroxy-ketone (IV) was, as Howe and McQuillin reported,[6] resistant to isomerization both by dilute acid and alkali. This is quite unlike its steroidal analogues which under these conditions readily yield 3,6-diones.[10] An enol-acetate (VII) was prepared but not fully characterized, and an attempt to prepare the corresponding 3,6-diones by its hydrolysis failed. However oxidation of the hydroxy-ketone (IV) with chromic



VII VIII IX

acid gave (+)-7β(H)-eudesma-4,11-dien-3,6-dione (IX),[6] which on reduction with zinc dust in acetic acid afforded two diketones, (X), m.p. 85–87°, and (XI), m.p. 126–127°, as the major product. Neither diketone was affected by hot dilute sulphuric acid, though both were isomerised in cold, dilute, methanolic potassium hydroxide solution to a new diketone, which almost certainly has the structure (XII). The fact that the isopropenyl group remains intact during the reduction of the ketone (IX) suggests that the stereochemistry at $C_{(7)}$ in the diketones (X) and (XI) must be the same as that in the ketone (IX). Had epimerization occurred at $C_{(7)}$ then a product containing



X XI XII

the conjugated carbonyl chromophore present in (XII) would have been expected. It was assumed as a working hypothesis, subsequently justified, that the reaction would leave the methyl group at $C_{(4)}$ with the more stable configuration.[3] The problem was therefore to decide the ring-fusion in each ketone. That, m.p. 126–127°, gave a rotatory dispersion curve with a molecular amplitude, $a = -67{\cdot}5$, and a circular dichroism curve, $\Delta\varepsilon_{303} - 1{\cdot}028$,* while that m.p. 85–87°, showed the extraordinarily large molecule amplitude, $a = +442$, and strong circular dichroism, $\Delta\varepsilon_{298} + 9{\cdot}97$. The IR and UV absorption spectra of the ketones were in no way abnormal. However due to the complexity of the rotatory dispersion curves of diketones,[11] no stereochemical deductions could be made with any certainty.

An attempt was therefore made to prepare the hydroxy-ketone (XIII) by reducing (+)-6β-hydroxy-7β(H)-eudesma-4,11-dien-3-one (IV) with lithium in liquid ammonia, a reaction which would be expected to give a *trans* ring-fusion. These conditions

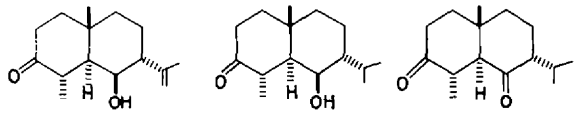
*$\Delta\varepsilon = \varepsilon_L - \varepsilon_D$, is the difference between the molecular absorption coefficients for right- and left-handed circularly polarized light. M. Legrand and R. Viennet, *Bull. Soc. Chim. Fr.* 1435 (1962); A. Lacam and *Ibid.* 1974 (1961); L. Velluz and M. Legrand, *Angew. Chem.* 73, 603 (1961).

[9] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* p. 84. Pergamon (1958); E. O. Bishop, *Ann. Reports* **58**, 58 (1961).

[10] L. F. Fieser and M. Fieser, *Steroids* p. 202. Reinhold, New York (1959).

[11] C. Djerassi and W. Closson, *J. Amer. Chem. Soc.* **78**, 3761 (1956).

resulted largely in the recovery of unchanged starting material (IV), and only a low yield the hydroxy-ketone (XIII), m.p. 157–158°. More vigorous conditions, lithium in ethylamine at 0°, afforded both the hydroxy-ketone (XIII) and the fully saturated hydroxy-ketone (XIV), m.p. 149–150°. In both reactions hydrogenolysis to (+)-7β(H)-eudesma-4,11-dien-3-one (V) was observed. The reduction of terminal olefinic linkages, though rare, is known.[12] A *trans* ring-fusion for these reduction

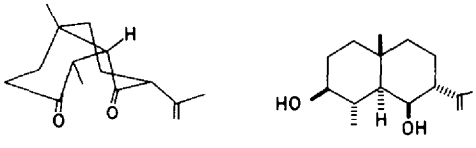


XIII XIV XV

products was supported by optical rotatory dispersion measurements (for XIII, $a = +69{\cdot}5$!).

The oxidation of these hydroxy-ketones with chromic acid proceeded very rapidly at 0° to give the diketones (X), m.p. 85–87°, and (XV), m.p. 113–114°. This result suggested the stereochemistry of the diketones (X) and (XI) obtained by the zinc-acetic acid reduction of (+)-7β(H)-eudesma-4,11-dien-3,6-dione (IX). The diketone, m.p. 126–127°, must possess the *cis* ring-fusion (XI), while that, m.p. 85–87°, must be assigned the *trans* ring-fusion (X).

The problem which remains is to account for the abnormal rotatory dispersion and circular dichroism curves of the diketone (X). A comparison with the recently reported steroid analogues[3] is not very telling, since the conformations of the ketones (X) and (XI) would undoubtedly be influenced by the 7α-isopropenyl group. In particular, the conformation of the diketone (XI) would probably be non-steroidal.[5,6,13] No obvious signs of vicinal interaction between the carbonyl groups in either diketone was discovered from the IR or UV spectra. It is suggested that the abnormal rotatory dispersion and circular dichroism curves of the diketone (X) must be due to some conformational distortion in ring B caused by the large axial isopropenyl group. Such distortions leading to "twist" forms usually have pronounced effects upon rotatory dispersion curves.[13,14] A precedent for this particular case can be found in the rotatory dispersion curve of (+)-7β(H)-eudesma-4,11-dien-3-one (v) already referred to. Little more can be said in view of the complex optical properties of diketones.[11] The optical properties of the diketone (XI) are in no way egregious, and this is perhaps surprising since the molecule almost certainly exists in the non-steroidal conformation (XVI) in which the carbonyl groups have almost the same orientation in space. This would not be the case in a steroidal conformation for the diketone (XI), nor in the conformation of the *trans* fused diketone (X).



XVI XVII

[12] T. J. King, *J. Chem. Soc.* 898 (1951); H. Greenfield, R. A. Friedel and M. Orchin, *J. Amer. Chem. Soc.* **76**, 1258 (1954).

[13] C. Djerassi and W. Klyne, *J. Chem. Soc.* 4929 (1962).

[14] C. Djerassi and W. Klyne, *Proc. Natl. Acad. Sci. U.S.* **48**, 1093 (1962).

The reduction of (+)-6β-hydroxy-4β,7β(H)-eudesm-11-en-3-one (XIII) with lithium tri-t-butoxyaluminium hydride proceeded smoothly to give (+)-4β,7β(H)-3β,6β-dihydroxy-eudesm-11-ene (XVII), which was also obtained by reducing (+)-4β,7β(H)-eudesm-11-en-3,6-dione (X) with the same reagent. This reagent is known to reduce 3- and 6-keto-steroids to the corresponding 3β- and 6β-hydroxy-compounds.[15] The fact that the same diol was obtained from the hydroxy-ketone (XIII) and the diketone (X) confirms the stereochemistry of the ring-fusions in the diketones X and XI. Further it supports a 6β-configuration for the hydroxyl group in (+)-6β-hydroxy-7β(H)-eudesma-4,11-dien-3-one (IV).

EXPERIMENTAL

M.ps. are uncorrected. Specific rotations were determined for chloroform solutions at room temp unless otherwise stated. UV spectra were measured for ethanol solutions on a Unicam SP 700. IR spectra were measured with Perkin-Elmer spectrophotometers PE-21 and Infracord 137 with NaCl prisms. NMR spectra were obtained using an AEI RS2 instrument at 60 and 25 Mc/s. RD (rotatory dispersion) measurements were made in the laboratory of Professor W. Klyne, Westfield College, London, and C.D. (circular dichroism) curves were measured in the laboratory of Professor G. Ourisson, Strasbourg University.

Alumina used for chromatography refers to Peter Spence's Grade H, deactivated with 5% of 10% acetic acid unless otherwise stated. Pet. ether refers to the fraction, b.p. 60–80°, unless otherwise stated.

(—)-5β-*Hydroxy*-4β,7β(H)-*eudesm*-11-*en*-3-*one* (III)

This compound was prepared from (—)-dihydrocarbone using a modification[4] of the procedure described by McQuillin.[5] It crystallized from pet ether as prisms, m.p. 108°; $[\alpha]_D$ −46°(*c*, 3·9). IR spectrum (in Nujol): ν_{max} 3350, 1710, 1645, 893 cm^{-1}. Lit. records:[5] m.p. 106°; $[\alpha]_{5461}$ −54°(*c*, 4·14).

The *semicarbazone* crystallized from ethanol aq. as needles, m.p. 239–240° (dec) (Found: C, 65·2; H, 9·3; N, 14·5. $C_{16}H_{27}N_3O_2$ requires: C, 65·5; H, 9·2; N, 14·3%).

(+)-6β-*Hydroxy*-7β(H)-*eudesma*-4,11-*dien*-3-*one* (IV)

This compound was prepared in the way described by Howe and McQuillin.[6] It crystallized from pet. ether as prisms, m.p. 65–66°; $[\alpha]_D$ +76° (*c*, 2·0). IR spectrum (in Nujol): ν_{max} 3500, 1655, 1605, 1360, 1345, 1310, 1250, 1230, 1200, 1145, 1100, 1020, 990, 900, 735 cm^{-1}. RD in methanol*: $[\phi]_{600}$ +650°, $[\phi]_{500}$ +700°, $[\phi]_{400}$ +1150°, $[\phi]_{365}$ +2690°, $[\phi]_{335}$ −4490°! NMR spectrum in CCl_4 (1% tetramethylsilane): τ 5·05(S), 5·12(S), 5·56(S), 6·20(S), 7·56(M), 7·68(M), 8·17(S), 8·22(S), 8·59(S) at 60 Mc/s. (M multiplet; S singlet). Lit. records:[6] m.p. 63–64°; $[\phi]_{5461}$ +88·2° (*c*, 4·2).

The *semicarbazone* crystallized from ethanol aq. as plates, m.p. 203–204° (Found: C, 65·9; H, 8·3; N, 14·8. $C_{16}H_{25}N_3O_2$ requires: C, 66·0; H, 8·6; N, 14·4%).

Attempted isomerization of (+)-6β-*hydroxy*-7β(H)-*eudesma*-4,11-*dien*-3-*one* (IV)

A solution of the hydroxy-ketone (IV; 250 mg) and toluene-*p*-sulphonic acid (80 mg) in isopropenyl acetate (15 ml) was heated under reflux for 9 hr. Solid $NaHCO_3$ was added to the cooled solution and the product isolated with ether. Removal of the solvents left a pale yellow oil (240 mg), which was adsorbed on neutral alumina (10 g). Benzene–pet. ether (2:3) eluted the *enol-acetate* (VII) as a very viscous oil (110 mg). IR spectrum (natural film): ν_{max} 1750, 1650, 1225, 893 cm^{-1}. UV spectrum: λ_{max} 243 mμ (ε = 9400), 285 mμ (ε = 3300) (Found: C, 71·3; H, 8·6. $C_{19}H_{26}O_4$ requires: C, 71·7; H, 8·2%).

Benzene eluted the acetate (VIII; 100 mg) as an oil, n_D^{20} 1·5216. IR spectrum (natural film): ν_{max} 1745, 1675, 1610, 1215, 893 cm^{-1}. The *semicarbazone* crystallized from ethanol aq. as needless m.p. 216–128° (Found: C, 64·6; H, 8·0; N, 12·8. $C_{18}H_{27}N_3O_3$ requires: C, 64·9; H, 8·1; N, 12·6%). Lit records:[6] n_D^{17} 1·5210.

* [ϕ] refers to the molecular rotation.

[15] H. J. E. Loewenthal, *Tetrahedron* **6**, 269 (1959); O. H. Wheeler and J. L. Mateos, *Canad. J. Chem.* **36**, 1431 (1958); C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.* 3361 (1952).

Attempts to hydrolyse the enol-acetate (VII) with $NaHCO_3$ or by adsorption on active alumina at room temp. afforded products whose IR spectra showed only very feeble bands attributable to an unconjugated carbonyl group.

(+)-7β(H)-*Eudesma*-4,11-*dien*-3,6-*dione* (IX).

(+)-6β-Hydroxy-7β(H)-eudesma-4,11-dien-3-one (IV) (200 mg) in purified acetone (10 ml) was treated with 8 N chromic acid aq.[16] at 0° until an orange colour persisted. After 5 min, the product was recovered by dilution with water and isolation in ether. (+)-7β(H)-Eudesma-4,11-dien-3,6-dione was obtained as an oil (170 mg), b.p. 90–95°/0·1 mm (bath); n_D^{22} 1·5314; $[\alpha]_D$ +365° (*c*, 0·5). IR spectrum (natural film): ν_{max} 1670, 1645, 1230, 1200, 935, 893 cm^{-1}. Lit. records:[6] b.p. 100–102°/0·1 mm; n_D^{20} 1·5321; $[\alpha]_{5461}$ +399° (*c*, 2·42); ν_{max} 893 cm^{-1}.

The mono-2,4-dinitrophenylhydrazone crystallized from ethanol as needles, m.p. 198°. Lit. records:[6] m.p. 196–197°.

Zinc-acetic acid reduction of (+)-7β(H)-*eudesma*-4,11-*dien*-3,6-*dione* (IX)

A solution of (+)-7β(H)-eudesma-4,11-dien-3-6,dione (300 mg) in acetic acid (10 ml) was kept at 90° and Zn dust (2·5 g) added in small portions during 2 hr. The mixture was constantly agitated during this time. The solids were removed by filtration and the product was isolated by diluting the filtrate with water and extracting with ether. The product was obtained as a gum (250 mg) and was adsorbed on alumina (50 g).

Pet. ether-benzene (1:1) eluted (+)-4β,7β(H)-*eudesm*-11-*en*-3,6-*dione* (X) (60 mg), which crystallized from pet. ether (b.p. 40–60°) at −60° as needles, m.p. 85–87°; $[\alpha]_D$ +180° (*c*, 2·8). IR spectrum (in Nujol): ν_{max} 1705, 1645, 893 cm^{-1}. UV spectrum: λ_{max} 296 mμ (ε = 130). RD in methanol (*c*, 0·5): $[\phi]_{600}$ +500°, $[\phi]_{500}$ +1000°, $[\phi]_{400}$ +2500°, $[\phi]_{330}$ +19600°, $[\phi]_{275}$ −24600°. CD in dioxan (*c*, 0·034): $\Delta\varepsilon_{298}$ +9·97, $\Delta\varepsilon_{306}$ +9·54 (Found: C, 76·7; H, 9·3. $C_{15}H_{22}O_2$ requires: C, 76·9; H, 9·4%). The *mono*-2,4-*dinitrophenylhydrazone* crystallized from ethanol as yellow needles, m.p. 198° (Found: C, 61·1; H, 6·0; N, 13·2. $C_{21}H_{26}N_4O_5$ requires: C, 60·9; H, 6·3; N, 13·5%).

Benzene to benzene-ether (5:1) eluted (—)-4β,5β,7β(H)-*eudesm*-11-*en*-3,6-*dione* (XI; 140 mg), which crystallized from pet. ether as needles, m.p. 126–127°; [α] −9° (*c*, 1·5). IR spectrum (in Nujol): ν_{max} 1705, 1645, 893 cm^{-1}. UV spectrum: λ_{max} 288 mμ (ε = 67). RD in methanol (*c*, 0·5): $[\phi]_{600}$ −100°, $[\phi]_{500}$ −150°, $[\phi]_{400}$ −250°, $[\phi]_{317}$ −2720°, $[\phi]_{277}$ +4030°. CD in dioxan (*c*, 0·24): $\Delta\varepsilon_{308}$ −1·028 (Found: C, 76·5; H, 9·4. $C_{15}H_{22}O_2$ requires: C, 76·9; H, 9·4%). The *mono*-2,4-*dinitrophenylhydrazone* crystallized from ethanol as orange-yellow needles, m.p. 220–222° (Found: C, 61·0; H, 5·9; N, 13·1. $C_{21}H_{26}N_4O_5$ requires: C, 60·9; H, 6·3; N, 13·5%).

Attempted isomerization of the diketones (X and XI)

Both diketones were recovered unchanged from hot dil. (2%) ethanolic H_2SO_4.

On standing for 12 hr in 0·4 N methanolic KOH both diketones were isomerized to (+)-4β(H)-*eudesm*-7(11)-*en*-3,6-*dione* (XII), b.p. 100–110°/0·2 mm (bath); n_D^{20} 1·5125; $[\alpha]_D$ +40° (*c*, 2·1). IR spectrum (natural film): ν_{max} 1705. 1675, 1625 cm^{-1}. UV spectrum: λ_{max} 252 mμ (ε = 6500) (Found: C, 76·4; H, 9·5. $C_{15}H_{22}O_2$ requires: C, 76·9; H, 9·4%).

Reduction of (+)-6β-*hydroxy*-7β(H)-*eudesma*-4,11-*dien*-3-*one* (IV)

(a) With Li in liquid ammonia. (+)-6β-hydroxy-eudesma-4,11-dien-3-one (300 mg) was added in dry ether (15 ml) to a solution of Li (300 mg) dissolved in liquid ammonia (100 ml). The blue solution was stirred for 1 hr, when solid NH_4Cl was cautiously added to destroy the excess reagent. The product was isolated by extraction with ether as an oil (280 mg), which was adsorbed on alumina (40 g).

Benzene eluted (+)-7β(H)-eudesma-4,11-dien-3-one (V) (40 mg) identified by its IR spectrum and 2,4-dinitrophenylhydrazone, m.p. 201°. Lit. records:[5] m.p. 202°.

Benzene–ether (5:1) eluted (+)-6β-*hydroxy*-4β,7β(H)-*eudesm*-11-*en*-3-one (XIII; 25 mg), which crystallized from pet. ether as needles, m.p. 157–158°; $[\alpha]_D$ +17° (*c*, 2·0). IR spectrum (in Nujol) ν_{max} 3340, 1705, 1640, 893 cm^{-1}. RD in methanol (*c*, 0·5): $[\phi]_{600}$ +75°, $[\phi]_{500}$ +100°, $[\phi]_{400}$ +125°, $[\phi]_{305}$ +2150°, $[\phi]_{275}$ −4800! (Found: C, 76·0; H, 10·0. $C_{15}H_{24}O_2$ requires: C, 76·3; H, 10·2%).

[16] A. Bowers, T. G. Halsall, E. R. H. Jones and A. J. Lemin, *J. Chem. Soc.* 2548 (1953).

Benzene–ether (4:1) eluted (+)-6β-hydroxy-7β(H)-eudesma-4,11-dien-3-one (IV; 165 mg), which crystallized from pet. ether as prisms, m.p. 65–67°.

(b) With Li in ethylamine. (+)-6β-Hydroxy-7β(H)-eudesma-4,11-dien-3-one (IV; 400 mg) was added in dry ether (20 ml) to a solution of Li (250 mg) in anhydrous ethylamine (50 ml) at 0°. The blue solution was stirred at 0° for 1 hr, when the excess reagent was destroyed by the cautious addition of solid NH_4Cl. Isolation with ether afforded a partly crystalline product (370 mg), which was adsorbed on alumina (50 g).

Benzene eluted (+)-7β(H)-eudesma-4,11-dien-3-one (V; 210 mg) identified as in (a) above.

Benzene–ether (9:1) eluted (+)-6β-*hydroxy*-4β,7β(H)-*eudesman*-3-*one* (XIV; 50 mg), which crystallized from pet. ether as very long needles, m.p. 149–150°; $[\alpha]_D$ +12° (*c*, 4·0). IR spectrum (in Nujol): ν_{max} 3350, 1705 cm^{-1} (Found: C, 75·3; H, 10·8. $C_{15}H_{26}O_2$ requires: C, 75·6; H, 10·9%).

Continued elution with benzene–ether (9:1) afforded (+)-6β-hydroxy-4β,7β(H)-eudesm-11-en-3-one (XIII: 75 mg), m.p. 157–158°.

(+)-4β,7β(H)-*Eudesman*-3,6-*dione* (XV)

(+)-6β-Hydroxy-4β,7β(H)-eudesman-3-one (XIV; 50 mg) was oxidized with 8 N H_2CrO_4 in acetone at 0° in the usual way.[16] The product, (+)-4β,7β(H)-*eudesman*-3,6-*dione* (XV; 35 mg), crystallized from pet. ether as prisms, m.p. 113–114°; $[\alpha]_D$ +156° (*c*, 1·7). IR spectrum (in Nujol): ν_{max} 1705, 1380, 1365 cm^{-1} (Found: C, 76·0; H, 9·8. $C_{15}H_{24}O_2$ requires: C, 76·3; H, 10·2%).

The oxidation of (+)-6β-*hydroxy*-4β,7β(H)-*eudesm*-11-*en*-3-*one* (XIII)

The hydroxy-ketone (XIII) was oxidized in the usual way with 8 N H_2CrO_4 in acetone at 0° to give (+)-4β,7β(H)-eudesm-11-en-3,6-dione (X) as needles, m.p. 85–87°, identical with the diketone obtained in the zinc-acetic acid reduction of (+)-7β(H)-eudesma-4,11-dien-3,6-dione (IX).

(+)-4β,7β(H)-3β,6β-*Dihydroxy-eudesm*-11-*ene* (XVII)

(a) Dry t-butanol (1 ml) was added at 0° to a solution of $LiAlH_4$ (100 mg) in tetrahydrofuran (10 ml).[15] To this solution at 0° was added a solution of (+)-6β-hydroxy-4β,7β(H)-eudesm-11-en-3-one (XIII; 50 mg) in tetrahydrofuran (2 ml), and the mixture left at 20° for 2 hr. Recovery by the addition of acetone and an aqueous solution of tartaric acid and then extraction with ether gave (+)-4β,7β(H)-3β,6β-*dihydroxy-eudesm*-11-*ene* (XVII) (30 mg), which crystallized from benzene–pet. ether (1:1) as needles, m.p. 166–167°; $[\alpha]_D$ +10° (*c*, 2·1) (Found: C, 75·2: H, 10·9. $C_{15}H_{26}O_2$ requires: C, 75·6; H, 10·9%).

(b) Reduction of (+)-4β,7β(H)-eudesm-11-en-3,6-dione (X) with the same reagent also gave the diol (XVII), m.p. 166–167°.

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