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SESQUITERPENOIDS—III

THE CHEMISTRY OF SOME 6-OXYGENATED EUDESMANES AND THE ABSOLUTE CONFIGURATION OF JUNENOL

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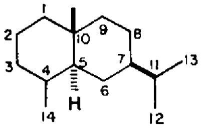
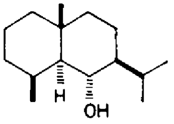
Abstract—The synthesis of dihydrojunenol (II) from (−)-5β-hydroxy-4β,7β(H)-eudesman-3-one (III) is reported, and the absolute configuration of junenol itself therefore confirmed as V. A method of removing the oxygen function at position 3 in 3,6-dioxygenated eudesmanes is described.

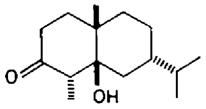
THE earlier papers in this series[1] described the chemistry of some eudesm-11-en-3,6-diones and some eudesman-3,6-diones. This paper reports the synthesis of dihydrojunenol (II) from (−)-5β-hydroxy-4β,7β(H)-eudesman-3-one (III) *via* (+)-7β(H)-eudesm-4-en-3,6-dione (IV). The nomenclature as in the previous papers, is based upon the eudesmane (I) of known absolute configuration.



I

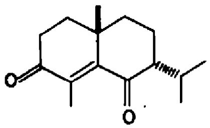


II

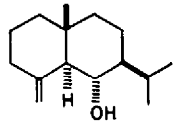


III

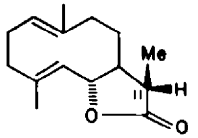
The naturally-occurring sesquiterpene alcohol junenol (V) has been investigated by several groups of workers,[2] and its absolute configuration has recently been established by the synthesis of junenol from dihydrocostunolide (VI) *via* the lactone (VII), and by the synthesis of dihydrojunenol (II) from "santanolide c" (VIII).[3] The synthesis of dihydrojunenol which is described here from the ketol with the



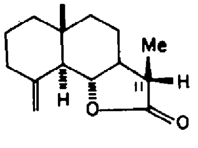
IV



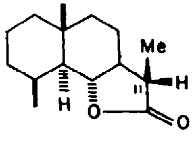
V



VI



VII



VIII

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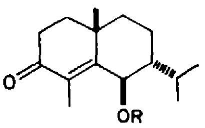
[1] D. W. Theobald, *Tetrahedron* **19**, 2261 (1963); **20**, 1455 (1964).

[2] V. Herout, O. Motl and F. Šorm, *Coll. Czech. Chem. Comm.* **22**, 785 (1957); S. C. Bhattacharyya, A. S. Rao and A. M. Shaligram, *Chem. & Ind.* 469 (1960).

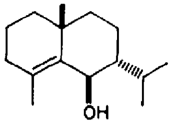
[3] A. H. Shaligram, A. S. Rao and S. C. Bhattacharyya, *Tetrahedron* **18**, 969 (1962).

known absolute configuration (III), therefore confirms the absolute configuration of junenol as that shown in V.

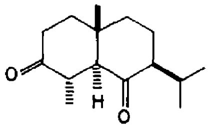
The crystalline ketol (III) of known absolute configuration[4] was chosen as the point of departure for this work, since a reliable method is known for introducing an oxygen function at position 6. This is fortunately not so for its 7α(H)-epimer, which might seem *prima facie* to be a more convenient starting material in that the $C_{(7)}$ centre would then have the correct stereochemistry from the beginning.[5] The action of oxygen in the presence of sodium isopropoxide at 80° converts the ketol (III) into (+)-6β-hydroxy-7β(H)-eudesm-4-en-3-one (IX; R=H) in 50% yields.



IX R=H ; R=Ac



X



XI

To arrive at the absolute stereochemistry of dihydrojunenol (II) from the stereochemistry present in the hydroxy-ketone (IX; R=H) required methods for (i) removing the oxygen function at position 3, (ii) the introduction of a *trans* ring-fusion, (iii) the introduction of a 4β-methyl group, and (iv) the epimerization of the 7α-isopropyl group to the 7β-position. Given an oxygen function at position 6, the epimerization stage (iv) presented no serious problems which had not already been explored.[1,5] The base-catalysed isomerization of the 7β(H)-ketone (IV) to its 7α(H)-epimer had previously been investigated.[1] And it seemed quite likely that straightforward hydrogenation of a 4:5-double bond, would, as long as the 7-isopropyl group occupied the 7β-position, lead directly to the desired stereochemistry at positions 4 and 5 (i.e. 4β-methyl and 5α-hydrogen). In fact the main problem was to find a successful method of removing the oxygen function at position 3, and the attempts to do this will now be outlined.

The Wolff–Kischner reaction failed to produce any material which could be characterized as the alcohol (X), indeed the product isolated after the high-temperature stage of the reaction still contained nitrogen. Hydroxy-ketones and steroid enones are known to frequently give complex products under such conditions.[6] Subsequently it was found that the hydroxy-ketone (IX; R=H) itself did not survive refluxing with potassium hydroxide in aqueous ethylene glycol at 130°. It appeared to be converted in part into hydroxylated material (IR spectrum: ν_{max} 3400, 1705 cm^{-1}) which could not be characterized, and in part to ketonic material (IR spectrum: ν_{max} 1710 cm^{-1}) from which a small quantity ($\simeq$ 5%) of (−)-4β(H)-eudesman-3,6-dione (XI)[1] was isolated by careful chromatography.

An attempt was therefore made to remove the oxygen function at position 3 by thioketalization and subsequent hydrogenolytic desulphurization with Raney nickel,

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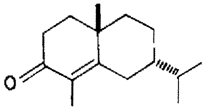
[4] F. J. McQuillin, *J. Chem. Soc.* 528 (1955); R. Howe and F. J. McQuillan, *Ibid.* 2423 (1955); 2670 (1956).

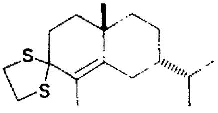
[5] H. M. E. Cardwell and F. J. McQuillin, *J. Chem. Soc.* 525 (1955); R. Howe and F. J. McQuillin, *Ibid.* 1513 (1958).

[6] L. F. Fieser and M. Fieser, *Steroids* p. 255. Reinhold, New York (1959).

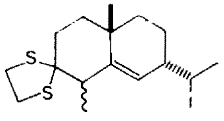
and this proved successful. It was found that ethanedithiol in glacial acetic acid to which boron trifluoride etherate had been added, gave very high yields of the ethylenethioketals at room temperature.[7] For example (+)-7β(H)-eudesm-4-en-3-one (XII) obtained by the dehydration of the ketol (III) in ethanolic hydrochloric acid, gave the crystalline ethylenethioketal (XIII) under these conditions. The hydroxyl group in the ketol (III) did not however survive these reaction conditions, and a mixture of the ethylenethioketals (XIII and XIV) in the ratio approximately 1:7 respectively, was obtained. This result suggests that the rate of thioketalization of the $C_{(3)}$ carbonyl group is at least as great as the rate of dehydration of the ketol in this reaction medium, for if the rate of dehydration were much greater, the proportion of the ethylenethioketal (XIII) would be expected to be greater. Two conformations, (XV and XVI), seem most likely for the probable intermediate hydroxy-ethylenethioketal. It is evident that of these XV is clearly to be preferred on the grounds of fewer and less serious non-bonded steric interactions; and the dehydration of XV will preferentially give the ethylenethioketal (XIV).



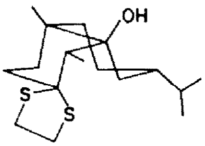
XII



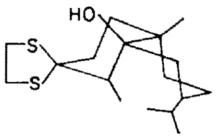
XIII



XIV

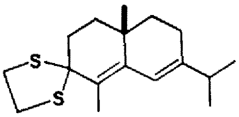


XV

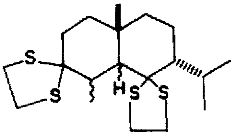


XVI

In view of these results it was perhaps not surprising that the hydroxyl group in the hydroxy-ketone (IX; R = H) did not survive attempts to make the ethylenethioketal of this compound. Unfortunately it also transpired that acetylation of the hydroxyl group afforded no protection, for the same products were obtained whether the starting material was the hydroxy-ketone (IX; R = H) or its acetate (IX; R = Ac). These products were in fact two; one, the crystalline ethylenethioketal (XVII), and two, a viscous oil whose structure is as yet undetermined. The NMR spectrum of this latter indicated the absence of vinylic protons, the UV spectrum the absence of conjugation, and the IR spectrum the absence of oxygen functions. Analysis figures were compatible with the molecular formula $C_{19}H_{32}S_4$ for a structure such as XVIII,



XVII



XVIII

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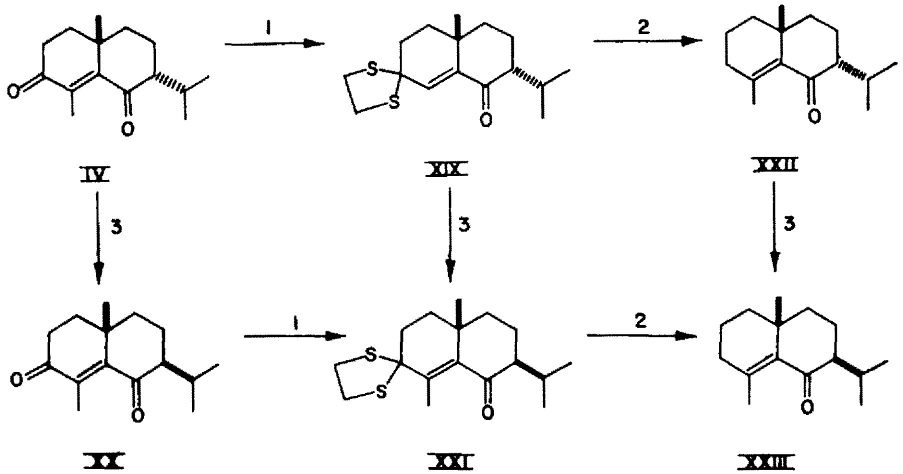
[7] P. N. Rao and H. R. Gollberg, *Tetrahedron* **18**, 1251 (1962).

and this possibility is now under investigation. If this structure should prove correct, it will be interesting in view of the fact that neither 6α- nor 6β-acetoxy-cholest-4-en-3-one under these conditions yield the di-ethylenethioketal of cholestan-3,6-dione.[8]

However (+)-7β(H)-eudesm-4-en-3,6-dione (IV) when treated with 1 equivalent of ethanedithiol in the presence of boron trifluoride etherate in acetic acid, gave the crystalline mono-ethylenethioketal (XIX), m.p. 105°, in very high yield. The same selective thioketalization has been observed with steroidal 4-en-3,6-diones.[9] The diketone (IV) was isomerized in ethanolic potassium hydroxide solution to its 7α(H)-epimer (XX)[1], and this diketone was treated with 1 equivalent of ethanedithiol under the same conditions. The mono-ethylenethioketal (XXI), m.p. 94–95°, was obtained. This compound was also obtained by treating the mono-ethylenethioketal (XIX) with ethanolic potassium hydroxide solution, which shows that during the formation of these ethylenethioketals, the carbonyl group at $C_{(6)}$ is not attacked and the stereochemistry at $C_{(7)}$ is preserved. In fact the carbonyl group at $C_{(6)}$ in all the compounds described in this paper was inert towards the usual carbonyl reagents.



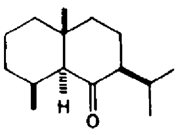
1. $(CH_2SH)_2/BF_3{\cdot}Et_2O/HOAc$ 2. Raney Ni 3. $KOH/EtOH/H_2O$

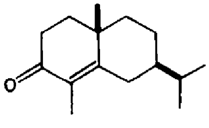
The mono-ethylenethioketal (XIX) was successfully desulphurized hydrogenolytically by refluxing with deactivated Raney nickel in ethanol[9] to give mainly (+)-7β(H)-eudesm-4-en-6-one (XXII). Some concomitant saturation of the 4:5-double bond was also observed (≏ 30%). The ketone (XXII) was then converted to (+)-eudesm-4-en-6-one (XXIII) by base-catalysed epimerization of the $C_{(7)}$ asymmetric centre. That this epimerization had indeed occurred was shown by the preparation of the ketone (XXIII) by the hydrogenolytic desulphurization of the mono-ethylenethioketal (XXI). A greater degree of saturation of the 4:5-double bond was observed in this desulphurization than in that of the mono-ethylenethioketal (XIX). This is not unexpected in view of the fact that the double bond in XXI and XXIII is considerably more exposed than that in XIX and XXII, where it is protected from hydrogenation not only by the 10β-methyl group, but also by the 7α-isopropyl group.

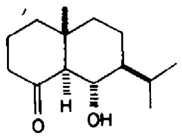
[8] L. F. Fieser and R. Stevenson, *J. Amer. Chem. Soc.* **76**, 1728 (1954).
[9] L. F. Fieser, *J. Amer. Chem. Soc.* **76**, 1945 (1954).

It was thought likely that direct hydrogenation of the ketone with the stereochemistry shown in XXIII would yield in the main a saturated ketone with the stereochemistry (XXIV) arising from hydrogenation on the α-face of the molecule (XXIII). This in fact proved to be the case, for from the hydrogenation product of the ketone (XXIII), a solid saturated ketone (XXIV), m.p. 33–34°, $[\alpha]_D$ +6·0°, was isolated, whose physical constants were close to those recorded by Sorm *et al.*[2] for the ketone obtained by direct oxidation of dihydrojunenol (II). Reduction of this ketone (XXIV) with sodium in ethanol gave a crystalline alcohol, m.p. 114–115°, $[\alpha]_D$ ±0°, identical (m.m.p., IR spectrum and $[\alpha]_D$) with an authentic specimen of dihydrojunenol.* Oxidation of dihydrojunenol with 8N chromic acid in acetone regenerated the ketone (XXIV).

These results confirm the absolute configuration already established for junenol (V),[3] at least as far as positions 7 and 10 are concerned. These positions therefore have the same absolute stereochemistry as (+)-α-cyperone (XXV) and most other sesquiterpenes in the eudesmane series.[10] But the results presented here do not allow the conclusion that the ring-fusion in junenol is *trans*, since the stereochemistry introduced at $C_{(5)}$ during the hydrogenation of the ketone (XXIII), although very likely to be that shown in XXIV, is not thereby proved to be such. However the positive Cotton effect (a = +40) of the ketone (XXIV) and the negative Cotton effect (a = −71) of the ketol (XXVI)[3,11] are best accommodated by octant diagrams arising from a *trans* ring-fusion in these compounds and so in junenol itself.


XXIV


XXV


XXVI

EXPERIMENTAL

M.ps. are uncorrected. Specific rotations were determined for chloroform solutions at room temp. 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 measured on a Perkin-Elmer R 10 at 60 Mc/s.

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

(−)-*5β-Hydroxy-4β*(H)-*eudesman-3-one* (III). This compound was prepared as described by McQuillin.[4] It crystallized from pet. ether as prisms, m.p. 65–66°; $[\alpha]_D$ −50° (*c*, 1·6). Lit. records[4]: m.p. 64–65°; $[\alpha]_{5461}$ −57° (*c*, 3·8).

(+)-*6β-Hydroxy-7β*(H)-*eudesm-4-en-3-one* (IX; R = H). This was prepared by the method described by McQuillin.[5] It crystallized from pet. ether (b.p. 30–40°) as prisms, m.p. 91°; $[\alpha]_D$ +26° (*c*, 3·2). Lit. records[5]: m.p. 90–91°; $[\alpha]_{5461}$ +27·2° (*c*, 3·5).

Attempted Wolff-Kischner reduction of the hydroxy-ketone (IX). The ketone (IX; R = H; 250 mg), KOH (1·0 g) and 99% hydrazine hydrate (2·0 ml) were refluxed in ethylene glycol (15 ml) for 3 hr under N_2. Excess hydrazine and water were boiled away until the internal temp. of the mixture

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* This was kindly supplied by Professor S. C. Bhattacharyya, National Chemical Laboratory, Poona, India.

[10] W. Cocker and T. B. H. McMurry, *Tetrahedron* **8**, 181 (1960).

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

reached 195°, and the mixture was then held at this temp for 5 hr. The mixture was cooled, diluted with water and the product recovered in ether. Lassaigne tests indicated that N_2 was present in the products.

When the first stage of the reaction was carried out with the quantities indicated above but in the absence of hydrazine, a yellow gum was obtained (230 mg). This was adsorbed on alumina (20 g). Pet. ether–benzene (1:1) eluted oily material (IR spectrum: ν_{max} 1710 cm^{-1}) (90 mg). Benzene–ether (5:1) eluted a gum (IR spectrum: ν_{max} 3400, 1710 cm^{-1}) (100 mg).

The pet. ether–benzene elutes were adsorbed on alumina (20 g). Elution with pet. ether–benzene (1:1) (100 ml) gave ten oily fractions; fractions 3 and 4 (20 mg) subsequently crystallized. The solid was recrystallized from pet. ether (b.p. 30–40°) to give XI (10 mg) as prisms, m.p. 47°, $[\alpha]_D$ −15° (*c*, 1·0). Lit. records[1]: m.p. 46–47°; $[\alpha]_D$ −17° (*c*, 3·0).

(+)-7β(H)-*Eudesm-4-en-3-one* (XII). This was prepared by the dehydration of the ketol (III) in ethanolic hydrochloric acid.[4] It was obtained as an oil, b.p. 105–106°/0·3 mm; n_D^{20} 1·5196; $[\alpha]_D$ +167° (*c*, 2·3). IR spectrum (natural film): ν_{max} 1675, 1615 cm^{-1}. UV spectrum: λ_{max} 251 mμ (ε = 14200). Lit. records[4]: b.p. 90°/0·1 mm; n_D^{20} 1·5190; $[\alpha]_{5461}$ +186° (*c*, 3·8); λ_{max} 250 mμ (log ε = 4·2).

The *semicarbazone* was obtained from ethanol aq. as plates, m.p. 190–191° (Found: C, 69·0; H, 9·6; N, 15·1. $C_{16}H_{27}N_3O$ requires: C, 69·3; H, 9·8; N, 15·2%).

The *ethylenethioketal* (XIII). A solution of the ketone (XII; 250 mg), ethanedithiol (0·3 ml) and boron trifluoride etherate (0·3 ml) in acetic acid (1 ml) was kept at 20° for 30 min. The product was isolated by dilution with water, neutralization with $NaHCO_3$ and extraction with ether. It was dissolved in pet. ether–benzene (10:1) and the solution filtered through alumina (10 g). The solid product obtained crystallized from methanol to give the *ethylenethioketal* (XIII) as prisms (240 mg), m.p. 93–94°; $[\alpha]_D$ +9·0° (*c*, 5·0). NMR spectrum in CCl_4 (1% $SiMe_4$) showed no vinylic protons (Found: C, 68·8; H, 9·3; S, 21·3. $C_{17}H_{28}S_2$ requires: C, 68·9; H, 9·5; S, 21·6%).

The ethylenethioketal (XIV). A solution of the ketol (III; 240 mg), ethanedithiol (0·3 ml) and boron trifluoride etherate (0·3 ml) in acetic acid (1 ml) was kept at 20° for 30 min. Recovery in the usual way gave the product as a gum (280 mg) which was adsorbed on alumina (60 g). Elution with pet. ether (30 ml) gave the ethylenethioketal (XIII; 30 mg) which crystallized from methanol as prisms m.p. 93–94°.

Further elution with pet. ether (60 ml) gave the *ethylenethioketal* (XIV; 220 mg) which crystallized from methanol at −10° as prisms, m.p. 37–38°; $[\alpha]_D$ +3·0° (*c*, 6·6). NMR spectrum in CCl_4 (1% $SiMe_4$) showed 1 vinylic proton at 4·70 ppm (J between the $C_{(8)}$-vinylic proton and the $C_{(7)}$-tertiary proton was ≃4 c/s) (Found: C, 68·9; H, 9·2; S, 21·2. $C_{17}H_{28}S_2$ requires: C, 68·9; H, 9·5; S, 21·6%).

The ethylenethioketals from the hydroxy-ketone (IX; R = H) *or its acetate* (IX; R = Ac). A solution of the hydroxy-ketone (IX; R = H; 300 mg), ethanedithiol (0·4 ml) and boron trifluoride etherate (0·3 ml) in acetic acid (1·5 ml) was kept at 20° for 1 hr. Recovery in the usual way gave the product as a gum (400 mg, which was adsorbed on alumina (70 g). Elution with pet. ether (40 ml) gave a *viscous oil* (possibly XVIII: 230 mg), n_D^{20} 1·5963; $[\alpha]_D$ +79° (*c*, 2·0). The UV spectrum showed no strong selective absorption; the NMR spectrum showed the absence of vinylic protons; and the IR spectrum showed the absence of hydroxyl and carbonyl functions (Found: C, 58·3; H, 8·0; S, 32·5. $C_{19}H_{32}S_4$ requires: C, 58·8; H, 8·3; S, 33·0%).

Further elution with pet. ether (30 ml) gave the *ethylenethioketal* (XVII; 90 mg) which crystallized from methanol at −10° as prisms, m.p. 45–46°; $[\alpha]_D$ +106° (*c*, 2·7). IR spectrum (in Nujol) ν_{max} 1615 cm^{-1}. UV spectrum: λ_{max} 244 mμ (ε = 12,200) (Found: C, 69·1; H, 8·6; S, 21·4. $C_{17}H_{26}S_2$ requires: C, 69·4; H, 8·8; S, 21·8%).

(+)-6β-*Acetoxy*-7β(H)-*eudesm-4-en-3-one* (IX; R = Ac). A solution of the hydroxy-ketone (IX; R = H; 400 mg) was heated under reflux in acetic anhydride (6 ml) and pyridine (1 ml) for 5 hr. The product was recovered by diluting the cooled mixture with water and ether, and washing the ethereal layer with $NaHCO_3$ solution and dil. HCl. It was adsorbed on alumina (20 g). Benzene eluted IX (R = Ac) as an oil (330 mg), b.p. 100–108°/0·1 mm (bath); n_D^{20} 1·5067; $[\alpha]_D$ +21° (*c*, 3·7). IR spectrum (natural film): ν_{max} 1745, 1670, 1610, 1240, 1020 cm^{-1}. UV spectrum: λ_{max} 251 mμ (ε = 14200) (Found: C, 73·2; H, 9·3. $C_{17}H_{26}O_3$ requires: C, 73·4; H, 9·4%).

The mono-ethylenethioketal (XIX). A solution of IV (380 mg), ethanedithiol (185 mg) and boron trifluoride etherate (2·2 ml) in acetic acid (27 ml) was kept at 20° for 19 hr. Recovery in the usual way gave the product as a gum, which crystallized from pet. ether (b.p. 30–40°) to give the *mono-ethylenethioketal* (XIX) as prisms (400 mg) m.p. 105°; $[\alpha]_D$ +245° (*c*, 1·6). IR spectrum (in Nujol): ν_{max} 1660, 1610 cm^{-1}. UV spectrum: λ_{max} 253 mμ (ε = 7200) (Found: C, 65·5; H, 8·1; S, 20·3. $C_{17}H_{26}OS_2$ requires: C, 65·8; H, 8·4; S, 20·6%).

It was not possible to prepare any carbonyl derivatives of this compound.

The mono-ethylenethioketal (XXI). Compound XX was prepared from its 7β(H)-epimer in the way already described.[1] A solution of the ketone (XX; 200 mg), ethanedithiol (100 mg) and boron trifluoride etherate (1·2 ml) in acetic acid (15 ml) was kept at 20° for 20 hr. Recovery in the usual way gave a gum which crystallized from pet. ether (b.p. 30–40°) at −10° to give the *mono-ethylenethioketal* (XXI) as prisms (190 mg), m.p. 94–95°; $[\alpha]_D$ +128° (*c*, 1·5). IR spectrum (in Nujol): ν_{max} 1665, 1615 cm^{-1}. UV spectrum: λ_{max} 253 mμ (ε = 6,700) (Found: C, 65·7; H, 8·2; S, 20·2. $C_{17}H_{26}OS_2$ requires: C, 65·8; H, 8·4; S, 20·6%).

It was not possible to prepare any carbonyl derivatives of this compound.

The isomerization of the mono-ethylenethioketal (XIX). A solution of XIX (200 mg) and KOH (1·5 g) in ethanol (20 ml) and water (3·0 ml) was kept under N_2 in the dark at 20° for 48 hr. Dilution with water and extraction with ether gave a solid product which was adsorbed on alumina (30 g). Elution with pet. ether–benzene (5:1; 60 ml) gave XXI which crystallized from pet. ether (b.p. 30–40°) as prisms (140 mg), m.p. 94–95°.

Further elution with the same solvent afforded XIX which crystallized from pet. ether (b.p. 30–40°) as prisms (35 mg), m.p. 105°.

(+)-7β(H)-*Eudesm-4-en-6-one* (XXII). Raney nickel (B.D.H. stabilized) was deactivated by refluxing in acetone for 3 hr. The mono-ethylenethioketal (XIX: 400 mg) was heated under reflux with deactivated Raney nickel (5 g) in ethanol (25 ml) for 5 hr. The catalyst was removed by filtration, and the filtrate evaporated to give an oil (260 mg). This was adsorbed on alumina (35 g). Elution with pet. ether (100 ml) gave an oil (70 mg), whose IR spectrum showed ν_{max} 1705 cm^{-1}. This was not further characterized.

Elution with pet. ether–benzene (5:1; 200 ml) gave XXII as an oil (160 mg), b.p. 95–98°/0·2 mm (bath); n_D^{20} 1·5176; $[\alpha]_D$ +132° (*c*, 2·8). IR spectrum (natural film): ν_{max} 1665, 1610 cm^{-1}. UV spectrum: λ_{max} 252·5 mμ (ε = 6900) (Found: C, 81·7; H, 10·6; $C_{15}H_{24}O$ requires: C, 81·8; H, 10·9%).

The $C_{(6)}$-carbonyl group was inert towards the usual carbonyl reagents.

(+)-*Eudesm-4-en-6-one* (XXIII). (a) The monoethylenethioketal (XXI; 400 mg) was heated under reflux with deactivated Raney nickel (5 g) in ethanol (25 ml) for 5 hr. The oily product (270 mg) was recovered in the usual way and adsorbed on alumina (35 g). Elution with pet. ether (150 ml) gave an oil (130 mg), whose IR spectrum showed ν_{max} 1710 cm^{-1}. This was not further characterized.

Elution with pet. ether–benzene (5:1; 150 ml) gave XXIII as an oil (100 mg), b.p. 95–100°/0·2 mm (bath); n_D^{20} 1·5150; $[\alpha]_D$ +72° (*c*, 3·2). IR spectrum (natural film): ν_{max} 1665, 1610 cm^{-1}. UV spectrum: λ_{max} 253 mμ (ε = 7400) (Found: C, 81·6; H, 10·8. $C_{15}H_{24}O$ requires: C, 81·8; H, 10·9%).

(b) A solution of XXII (900 mg) and KOH (6 g) in ethanol (60 ml) and water (12 ml) was kept under N_2 in the dark at 20° for 48 hr. Dilution with water and extraction with ether gave the product as an oil (870 mg), which was adsorbed on alumina (170 g). Elution with pet. ether–benzene (6:1; 15 × 20 ml) gave nearly pure XXIII (500 mg) as an oil, $[\alpha]_D$ +80° (*c*, 2·1).

Further elution with the same solvent (10 × 20 ml) gave a mixture (210 mg) of the epimers (XXII and XXIII).

Yet further elution with the same solvent (10 × 20 ml) gave nearly pure XXII (150 mg), $[\alpha]_D$ +122° (*c*, 2·0).

The first 15 fractions of this chromatogram, consisting of nearly pure XXIII (500 mg) were rechromatographed on alumina (80 g). Elution with pet. ether–benzene (6:1; 10 × 20 ml) gave pure XXIII (400 mg), $[\alpha]_D$ +74° (*c*, 4·0).

Further elution with the same solvent gave (+)-eudesm-4-en-6-one contaminated with its 7β(H)-epimer.

The $C_{(6)}$-carbonyl group in the ketone (XXIII) was inert towards the usual carbonyl reagents.

(+)-4α(H)-*Eudesman-6-one* (XXIV). Compound XXIII (600 mg) in ethanol with Pd-C (20%) took up 1·1 mole H_2 to give an oily product which was adsorbed on alumina (80 g). The material was eluted with pet. ether (500 ml) in 25 fractions. Fractions 14–23 (350 mg) crystallized on standing to give nearly pure XXIV, m.p. 28–30°. This material was rechromatographed on alumina (40 g) and was eluted with pet. ether (250 ml) in 25 fractions. Fractions 8–18 crystallized on standing as pure XXIV (300 mg), m.p. 33–34°; b.p. 95–97°/0·1 mm (bath); $[\alpha]_D$ +6·0° (*c*, 6·5). IR spectrum (in Nujol): ν_{max} 1705 cm^{-1} (Found: C, 81·0; H, 11·5. Calc. for $C_{15}H_{26}O$: C, 81·1; H, 11·7%). Lit. records[2]: m.p. 34·5°; $[\alpha]_D$ +5·8° (*c*, 5·69 in ethanol).

The $C_{(6)}$-carbonyl group was inert towards the usual carbonyl reagents.

Dihydrojunenol (4α(H)-6α-*hydroxy-eudesmane*) (II). (+)-4α(H)-Eudesman-6-one (XXIV; 150 mg) was dissolved in ethanol (10 ml) and Na (500 mg) added in small pieces under N_2 during 30 min. Recovery by dilution with water and extraction with ether gave solid material (140 mg). This was adsorbed on alumina (20 g) from which benzene–ether (5:1) eluted dihydrojunenol (95 mg), which crystallized from pet. ether (b.p. 30–40°) at −60° as small prisms, m.p. 114–115°; m.m.p. with authentic dihydrojunenol 114–115°; $[\alpha]_D$ +0°.