Tetrahedron. Vol. 24, pp. 5227 to 5240 Pergamon Press 1968. Printed in Great Britain

# SESQUITERPENOIDS—VII

## THE SYNTHESIS OF SOME 2-KETOEUDESMANES

D. L. ROBINSON† and D. W. THEOBALD*

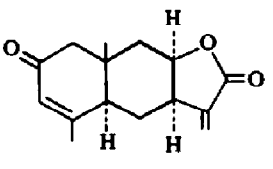
University of Manchester Institute of Science and Technology

(*Received in the UK* 5 *March* 1968; *accepted for publication* 21 *March* 1968)

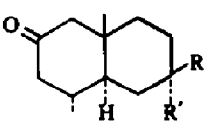
**Abstract**—A synthesis of some 2-ketoeudesmanes from the corresponding 3-ketoeudesmanes is described.

DESPITE considerable work on the synthesis of eudesmane sesquiterpenes there has to our knowledge been no attempt to construct the 2-ketoeudesmane system which occurs, for example, in pinnatifidin (I).[1] This paper is concerned generally with the exploration of a synthetic route to such a system, and in particular with the stereoselective syntheses of (+)-4β,7β(*H*)-eudesman-2-one (II) and (+)-4β(*H*)-eudesman-2-one (III). The nomenclature used in this paper is based on the hydrocarbon eudesmane (IV) of known absolute stereochemistry.

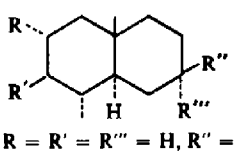
The ketol, (−)-5β-hydroxy-4β,7β(*H*)-eudesm-11-en-3-one (V) was chosen as a suitable point of departure in this investigation because of the ease with which it could be synthesized stereospecifically.[2] This ketol was converted to (−)-4β,7β(*H*)-eudesman-3-one (VI) following the procedure described by Howe and McQuillin.[3] It was proposed initially to move the C(3) keto-function of this compound to position C(2) *via* the bromohydrin-epoxide route which has been employed successfully in, for example, the syntheses of 4-demethyltetrahydroalantolactone[4] and 5α-cholestan-2α-ol.[5]



I



II: R = H, R′ = $^{i}$Pr
III: R = $^{i}$Pr, R′ = H



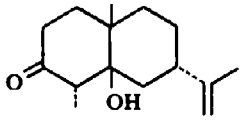
IV: R = R′ = R‴ = H, R″ = $^{i}$Pr
VIII: R′ = R″ = H, R′ = OH, R‴ = $^{i}$Pr
IX: R = R′ = OH, R″ = H, R‴ = $^{i}$Pr
XVI: R = OH, R′ = R″ = H, R‴ = $^{i}$Pr
XXXV: R = OH, R′ = R‴ = H, R″ = $^{i}$Pr

* To whom enquiries should be addressed.

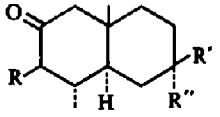
† Present address; The Dyson Perrins Laboratory, South Parks Road, Oxford.

As was expected by analogy with the steroids, kinetically controlled monobromination of (−)-4β,7β(*H*)-eudesman-3-one (VI) gave (−)-2α-bromo-4β,7β(*H*)-eudesman-3-one (VII).[6] The 2α-position of the Br atom was indicated by the CO frequency in the IR spectrum,[7] and the quartet at 5·25 τ in the NMR spectrum.[8] Analysis of this quartet revealed a slight flattening of the cyclohexanone ring in the bromoketone (VII).[9,10]

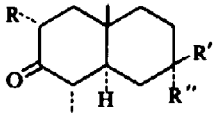
A small distortion of this nature was also suggested by optical rotatory dispersion evidence. The change in molecular amplitude observed in going from (−)-4β,7β(*H*)-eudesman-3-one (VI) to (−)-2α-bromo-4β,7β(*H*)-eudesman-3-one (VII) (Δa + 20) was greater than that observed in going from 5α-cholestan-3-one to 2α-bromo-5α-cholestan-3-one (Δa − 5·2).[11] It is likely that this distortion is caused by steric compression on the α-face of the molecule in conjunction with the electrostatic interaction between the equatorial Br atom and the CO group.




V




XI: R = OAc, R′ = H, R″ = $^{i}$Pr
XXXI: R = Ac, R″ = H, R′ = $^{i}$Pr




VI: R = R′ = H, R″ = $^{i}$Pr
VII: R = Br, R′ = H, R″ = $^{i}$Pr
X: R = OAc, R′ = H, R″ = $^{i}$Pr
XIX: R = R″ = H, R′ = $^{i}$Pr
XXIV: R = R′ = H, R″ = isopropenyl
XXVIII: R = R″ = H, R′ = isopropenyl
XXIX: R = Br, R″ = H, R′ = $^{i}$Pr
XXX: R = OAc, R″ = H, R′ = $^{i}$Pr

The reduction of (−)-2α-bromo-4β,7β(*H*)-eudesman-3-one (VII) with LAH did not give the expected bromohydrin, 2α-bromo-4β,7β(*H*)-eudesman-3β-ol. The products isolated from the reaction were identified as (−)-4β,7β(*H*)-eudesman-3ξ-ol (ξ probably β; VIII), the major product (≃65%), and (−)-4β,7β(*H*)-eudesman-2α,3β-diol (IX), the minor product (≃35%).

The alcohol (VIII) and the ketone (VI) were related by the usual oxidation and reduction reactions. The diol IX was identified on the basis of analytical and spectral data and also by its independent synthesis from (+)-2α-acetoxy-4β,7β(*H*)-eudesman-3-one (X). The high resolution IR spectrum obtained with a dilute solution of the diol in $CS_2$ displayed two OH absorption bands at 3612 and 3584 $cm^{-1}$. The first of these bands could be attributed to the presence of unbonded OH groups and the second to the presence of intramolecularly-bonded OH groups. The band separation $\Delta\nu = 28$ $cm^{-1}$ was approximately that expected[12] for a vicinal *trans*-diequatorial

diol ($\Delta\nu$ expected, 32 $cm^{-1}$) and suggested that the compound was 4β,7β(*H*)-eudesman-2α,3β-diol (IX). The identity of the compound was settled by its synthesis from the reduction of the acetoxy-ketone X with LAH.

Although the presence of the alcohol VIII amongst the products obtained in the reduction of (−)-2α-bromo-4β,7β(*H*)-eudesman-3-one can be explained by hydrogenolysis, the presence of the diol IX can be explained most easily by postulating the intermediate formation of a 2β,3β-epoxide,[13] which would be cleaved by the aqueous tartaric acid employed during the recovery procedure to give the observed diol.

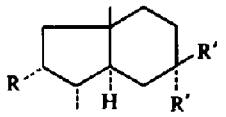
With the failure of the bromohydrin-epoxide route to 4β,7β(*H*)-eudesman-2-one it was decided to introduce an oxygen function at the C(2) position in (−)-4β,7β(*H*)-eudesman-3-one (VI) directly, and then to reduce the CO group to a methylene function.

The introduction of an oxygen function at the C(2) position of the ketone VI was achieved by the acetolysis of the bromo-ketone VII using anhydrous potassium acetate in glacial acetic acid. Chromatography of the reaction product on alumina gave two crystalline acetoxy-ketones which were identified, largely on the basis of their NMR spectra, as (+)-2α-acetoxy-4β,7β(*H*)-eudesman-3-one (X), m.p. 107°, the expected and major product, and (+)-3β-acetoxy-4β,7β(*H*)-eudesman-2-one (XI), m.p. 92–93°. The quartet ($J_{a,a} = 13{\cdot}0 \pm 0{\cdot}5$; $J_{a,e} = 7{\cdot}0 \pm 0{\cdot}5$ c/s) which appeared at 4·77 τ in the NMR spectrum of X, m.p. 107°, was attributed to the signal of the C(2)β-proton coupled with the two C(1)-protons.[14] The doublet ($J_{a,a} = 10$ c/s) which appeared at 5·35 τ in the NMR spectrum of XI, m.p. 92–93°, was attributed to the signal of the C(3)α-proton coupled with the lone C(4)β-proton.

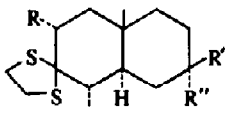
It was probable that (+)-2α-acetoxy-4β,7β(*H*)-eudesman-3-one (X) is the initial product in the acetolysis reaction and then rearranges to (+)-3β-acetoxy-4β,7β(*H*)-eudesman-2-one (XI) under the influence of the base present ($CH_3CO_2^-$). Similar rearrangements have been shown to occur with steroidal and triterpenoid analogues.[15,16] In these cases an equilibrium exists between the 2α-acetoxy-3-keto- and the 3β-acetoxy-2-keto-isomers. In the present case the 3β-acetoxy-2-keto-isomer appeared to be the more stable. When a pure sample of (+)-2α-acetoxy-4β,7β-(*H*)-eudesman-3-one was adsorbed on basic alumina, samples of both acetoxy-ketones could be isolated. A pure sample of (+)-3β-acetoxy-4β,7β(*H*)-eudesman-2-one treated under the same conditions was unaffected, and no (+)-2α-acetoxy-4β,7β(*H*)-eudesman-3-one could be isolated.

It was found that the acetoxy-ketone (X) could be obtained in higher overall yield from the ketone VI by direct acetoxylation with lead tetra-acetate in a mixture of benzene and methanol containing $BF_3$-etherate.[16] The NMR spectrum of the crude reaction product revealed the presence of only one acetoxy-ketone, (+)-2α-acetoxy-4β,7β(*H*)-eudesman-3-one (X), together with an unexpected by-product. This by-product was readily isolated by chromatography on alumina, and was identified as (−)-2α-methoxycarbonyl-3β,6β(*H*)-A-noreudesmane (XII). The IR ($\nu_{max}$: 1736, 1212, 1163 $cm^{-1}$), NMR (6·93τ, singlet —OMe) and mass spectra (M − 31; M − 59) clearly indicated that the compound was a methyl ester. The sextet which appeared at 7·07τ in the NMR spectrum of the compound was typical of the X proton in an $AM_2X$ system indicating the presence of the system $—CH_2—CH(CO_2CH_3)—CH<$ in the compound. On this basis and by analogy with a recent steroidal example[17]

the compound was assigned the structure XII. Reduction of the ester with ethereal LAH gave the corresponding alcohol (−)-2α-hydroxymethyl-3β,6β(*H*)-A-nor-eudesmane (XIII).




XII: R = $CO_2Me$, R′ = H, R″ = $^iPr$
XIII: R = $CH_2OH$, R′ = H, R″ = $^iPr$
XXXII: R = $CO_2Me$, R″ = H, R′ = $^iPr$




XIV: R = OAc, R′ = H, R″ = $^iPr$
XV: R = OH, R′ = H, R″ = $^iPr$
XVIII: R = R′ = H, R″ = $^iPr$
XXXIII: R = OAc, R″ = H, R′ = $^iPr$
XXXIV: R = OH, R″ = H, R′ = $^iPr$

An attempt was made to remove the 3-keto function of the acetoxyketone X by reducing its tosylhydrazone with sodium borohydride.[18] Although the tosylhydrazone of the ketone VI was obtained crystalline, that of the acetoxy-ketone X was isolated as a gum. The reduction of this with sodium borohydride yielded no product which could be satisfactorily characterized. The deacetoxylation of (+)-3β-acetoxy-4β,7β(*H*)-eudesman-2-one (XI) by refluxing with zinc in acetic acid was also unsuccessful.[19]

However the 3-keto function of (+)-2α-acetoxy-4β,7β(*H*)-eudesman-3-one was successfully removed by the hydrogenolytic desulphurization of its ethylenethioketal derivative with Raney Ni.[20] The acetoxyketone (X) in glacial acetic acid containing 1,2-ethanedithiol and $BF_3$-etherate afforded (+)-3,3-ethylenedithio-4β,7β(*H*)-eudesman-2α-ol acetate (XIV) in high yield.[21] In order to prevent excessive hydrogenolysis during the Raney Ni desulphurization the acetoxy-ethylenethioketal was first hydrolysed using methanolic potassium hydroxide.[20,22] The resultant hydroxy-ethylenethioketal, (+)-3,3-ethylenedithio-4β,7β(*H*)-eudesman-2α-ol (XV), was successfully desulphurized by refluxing over W-2 Raney Ni in acetone.[20,23] Chromatography on alumina gave three principal products; two oils and crystalline (−)-4β,7β(*H*)-eudesman-2α-ol (XVI), m.p. 76°. One of the oils was identified as an impure sample of (+)-4β,7β(*H*)-eudesman-2-one (II) by its IR spectrum. The presence of this compound amongst the reaction products could only be explained in terms of an exchange reaction between the solvent acetone and either the alcohol XVI, or more likely, the hydroxy-ethylenethioketal XV on the surface of the Raney Ni. A similar reaction has been observed in a steroidal example.[24] The other oil was not characterized, but its IR spectrum suggested that it was an olefin or a mixture of an olefin and a hydrocarbon.

The oxidation of the alcohol XVI with chromic acid at 0° gave a high yield of (+)-4β,7β(*H*)-eudesman-2-one (II).[25] The mass spectral fragmentation pattern of

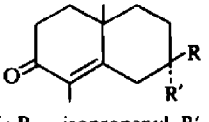
this ketone, which was similar to those of 5α-cholestan-2-one and 5α-androstan-2-one, confirmed the C(2)-location of the CO group. The prominent peak at *m/e* 164 (M − 58) probably arises from the expulsion of acetone.[26] As expected on the basis of the octant rule the ketone displayed a positive Cotton effect (a +55).[27] Further, the ORD maximum of the ketone appeared at 309 mμ whereas that of the acetoxy-ketone XI appeared at 302 mμ. The observed hypsochromic shift is typical of that associated with the introduction of an equatorial acetoxyl group α to a carbonyl function in a 6-membered ring.[28] Further evidence for the C(2)-location of the CO group was obtained from the mass spectrum of the ethylenethioketal (XVII). The prominent peak at *m/e* 145 could be accounted for only by assigning the structure 2,2-ethylenedithio-4β,7β(*H*)-eudesmane (XVII) to this compound. The fragmentation pattern exhibited by (−)-3,3-ethylenedithio-4β,7β(*H*)-eudesmane (XVIII) was completely different (base peak *m/e* 132).

This method for the conversion of a 3-keto-eudesmane to a 2-keto-eudesmane was applied to the synthesis of 4β(*H*)-eudesman-2-one (III). The initial problem was to obtain a large sample of optically pure (−)-4β(*H*)-eudesman-3-one (XIX). Howe and McQuillin[3] had previously converted (−)-5β-hydroxy-4β,7β(*H*)-eudesm-11-en-3-one (V) to the ketone XIX by two different routes. These routes have been reinvestigated, and the products compared with those obtained from the reduction of natural (+)-α-cyperone (XX).

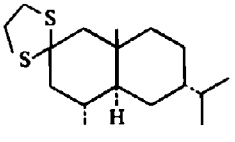
The ketol V was smoothly dehydrated in aqueous ethanolic hydrochloric acid at 0° to give (+)-epi-α-cyperone (XXI). Treatment of this compound with 50% v/v aqueous sulphuric acid at 0° induced a double-bond isomerization to give (+)-β-cyperone (XXII). The reduction of (+)-β-cyperone with zinc in acetic acid led to an oil which was separated into two components by careful chromatography on alumina. One of the oils proved to be the desired (−)-4β(*H*)-eudesman-3-one (XIX) and the other a partial reduction product, (+)-eudesm-4-en-3-one (XXIII).

The second route to (−)-4β(*H*)-eudesman-3-one (XIX) involved the reduction of (+)-epi-α-cyperone (XXI) with lithium in liquid ammonia. The product from this reaction, (+)-4β,7β(*H*)-eudesm-11-en-3-one (XXIV), was then hydrogenated over palladised charcoal to give the ketone XIX.

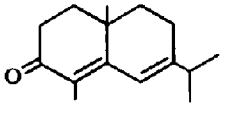
Howe and McQuillin[3] have shown that (+)-4β,7β(*H*)-eudesm-11-en-3-one (XXIV) undergoes isomerization when refluxed over Pd-C in neutral or acidified ethanol, and they suggested that the product might be the ketone XXV or more probably the




XX: R = isopropenyl, R' = H
XXI: R = H, R' = isopropenyl
XXIII: R = $^{i}$Pr, R' = H

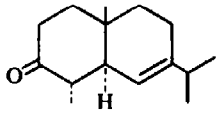



XVII

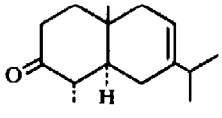



XXII

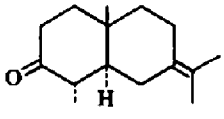
$\Delta^{7,8}$-ketone XXVI. During the present investigation, however, it was found that the product from this bond migration reaction contained both of the above ketones and the ketone XXVII with an isopropylidene side chain. The presence of these isomers was revealed by the NMR spectrum of the crude isomerization product. The multiplets at 4·66 and 5·36 τ, of approximately equal intensity, indicated vinylic protons in different magnetic environments and the presence of approximately equal proportions of the two ketones (XXV and XXVI) in the product. The intense singlet at 8·35 τ could be explained in terms of an isopropylidene group and so the presence of the ketone XXVII in the product. The signal at 8·35 τ was approximately twice as intense as the doublet at 9·05 τ associated with the isopropyl Me groups in the other two isomeric ketones, so that the product ratio of the three isomers XXV : XXVI : XXVII is approximately 1 : 1 : 4. These ketones were not separable by chromatography on alumina. In one chromatographic fraction, however, the intensities of the absorption bands at 809 and 843 $cm^{-1}$ in the IR spectrum were greatly reduced. It was on the basis of these absorption bands that Howe and McQuillin suggested the structure XXVI for the reaction product.[3]



XXV



XXVI



XXVII

For comparative purposes an authentic sample of (−)-4β(*H*)-eudesman-3-one (XIX) was prepared from natural (+)-α-cyperone (XX).[29] Reduction of this with lithium in liquid ammonia gave the *trans*-fused ketone VIII, which on hydrogenation over platinum in ethanol gave (−)-4β(*H*)-eudesman-3-one (XIX).

The low specific rotation of the saturated ketone made a direct comparison of the optical purities of the three samples difficult. They were consequently converted to their oximes. A comparison of these oximes showed clearly that the most convenient route to optically pure (−)-4β(*H*)-eudesman-3-one was that involving the reduction of (+)-epi-α-cyperone (XXI).

The optically pure oxime ($[\alpha]_D$ −116°) of (−)-4β(*H*)-eudesman-3-one (XIX) prepared from (+)-epi-α-cyperone (XXI) was hydrolyzed using oxalic acid in aqueous methanol in the presence of formaldehyde and light petroleum. The ketone XIX so secured was optically pure and was used in all subsequent reactions.

The kinetically controlled monobromination of (−)-4β(*H*)-eudesman-3-one (XIX) gave 2α-bromo-4β(*H*)-eudesman-3-one (XXIX) as an unstable oil. The CO absorption at 1724 $cm^{-1}$ showed a hypsochromic shift of 15 $cm^{-1}$ from the CO absorption of the parent ketone (1709 $cm^{-1}$). The instability of the compound prevented any other spectral data being recorded.

The kinetically controlled monobromination of the ketone XIX proceeded much more rapidly than that of its 7β(*H*)-epimer (VI). This difference suggests that the $\Delta^2$-enol in the former ketone is more easily produced than in the latter. On the basis of the argument suggested earlier this difference might be expected because (−)-4β(*H*)-eudesman-3-one (XIX), in which the bulky isopropyl group possesses an equatorial configuration, should be free from steric compression on its α-face.

As in the case of (−)-4β,7β(*H*)-eudesman-3-one (VI) the acetoxylation of (−)-4β(*H*)-eudesman-3-one (XIX) using lead tetra-acetate and $BF_3$ in a mixture of benzene and methanol led to several products.[16] Chromatography of the reaction product on alumina gave (+)-2α-acetoxy-4β(*H*)-eudesman-3-one (XXX), m.p. 52–53°, and two oils. The nuclear magnetic resonance spectrum of the compound m.p. 52–53° displayed a quartet ($J_{a,a}$ = 13·0 ± 0·5; $J_{a,e}$ = 7·0 ± 0·5 c/s) at 4·77 τ, which, as in the case of the acetoxy-ketone (X) was attributed to the signal of the C(2)β-proton. The equatorial orientation of the acetoxyl group was confirmed by comparing the ORD maximum of the acetoxy-ketone (305 mμ) of the parent ketone XIX.[28] One of the oils was identified as (+)-3β-acetoxy-4β(*H*)-eudesman-2-one (XXXI). The NMR spectrum of this ketone, which was quite similar to that of the acetoxy-ketone XI exhibited a doublet ($J_{a,a}$ = 10 c/s) at 5·30 τ which was attributed to the signal of the C(3)α-proton. The other oil isolated from the acetoxylation reaction was identified as the ring contraction ester, (−)-2α-methoxycarbonyl-3β(*H*)-A-noreudesmane (XXXII) whose spectral characteristics were very similar to those of (−)-2α-methoxycarbonyl-3β,6β(*H*)-A-noreudesmane (XII).

Following the procedure employed in the 7β(*H*)-series, (+)-2α-acetoxy-4β(*H*)-eudesman-3-one (XXX) was converted in high yield to its ethylenethioketal derivative (XXXIII). Hydrolysis gave the corresponding hydroxy-ethylenethioketal (XXXIV) which was desulphurized by refluxing over W-2 Raney Ni in acetone. Chromatography on alumina gave three products all of which were oils.

The major product was identified as 4β(*H*)-eudesman-2α-ol (XXXV) (IR $\nu_{max}$: 3344, 1025 $cm^{-1}$) which upon oxidation with chromic acid gave (+)-4β(*H*)-eudesman-2-one (III). The mass spectral fragmentation pattern of this ketone (prominent peaks at *m/e* 164, *m/e* 95), which was practically identical to that of (+)-4β,7β(*H*)-eudesman-2-one (II), confirmed the C(2)-location of the CO group, further support for which was obtained from the ORD persion curve which, as expected on the basis of the octant rule, displayed a positive Cotton effect (a + 46).[27]

## EXPERIMENTAL

M.ps are uncorrected. Specific rotations were determined for $CHCl_3$ solns at room temp. IR spectra were measured with Perkin–Elmer spectrophotometers PE-21 and Infracord 137 with NaCl optics. NMR spectra were obtained using a Perkin–Elmer R10 at 60 Mc/s. The following symbols have been used to classify types of signals: S- singlet; D- doublet; Q- quartet; Sex- sextet; Sep- septet; M- unspecifiable multiplet. Mass spectra were measured on an AEI MS 10 instrument. Rotatory dispersion measurements were made in the laboratory of Professor W. Klyne, Westfield College, London.

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

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

This compound was prepared from (−)-dihydrocarvone using the procedure described by Halsall, *et al.*[26] It crystallized from pet. ether as prisms, m.p. 106°; $[\alpha]_D$ −47° (*c*, 2·09); IR spectrum (in $CCl_4$): $\nu_{max}$ 3636, 1709, 1642, 892 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 5·37 (D); 7·22 (Q); 8·22 (S);

8·79 (S); 9·04 (D); mass spectrum: parent ion *m/e* 236, base peak *m/e* 109; Lit. records:[26] m.p. 106°; $[\alpha]_{5461}$ −54° (*c*, 4·14).

(−)-4β,7β(H)-*Eudesman*-3-*one* (VI)

This compound was prepared from (−)-5β-hydroxy-4β,7β(*H*)-eudesm-11-en-3-one in the way described by Howe and McQuillin.[3] It crystallized from pet ether (b.p. 40–60°) as colourless prisms, m.p. 66–67°; $[\alpha]_D$ −6·5° (*c*, 7·5); IR spectrum (in $CCl_4$): $\nu_{max}$ 1709, 1377, 1359 $cm^{-1}$. NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 8·88 (S); 9·10 (D); RD (in MeOH): $[\phi]_{303}$ +1932°, $[\phi]_{263}$ −3886°, $[\phi]_{236}$ −3242°, $[\phi]_{214}$ −4329°; mass spectrum: parent ion *m/e* 222, base peak *m/e* 55; Lit. records:[3] m.p. 66–67°; $[\alpha]_{5461}$ −4·6° (*c*, 7·6).

(−)-2α-*Bromo*-4β,7β(H)-*eudesman*-3-*one* (VII)

Compound VI (222 mg) in AcOH (15 ml) was treated with one drop of a saturated soln of HBr in AcOH, and then dropwise with a soln of $Br_2$ (170 mg) and anhyd NaOAc (86 mg) in AcOH (10 ml). Recovery in ether gave (−)-2α-*bromo*-4β,7β(H)-*eudesman*-3-*one* which crystallized from pet ether (b.p. 40–60°) as colourless prisms (150 mg), m.p. 119–120°; $[\alpha]_D$ −24·7° (*c*, 5·37); IR spectrum (in $CCl_4$): $\nu_{max}$ 1730, 1385, 1379, 1365 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 5·25 (Q); 8·79 (S); 8·97 (D); 9·10 (D); 9·14 (D); RD (in MeOH): $[\phi]_{305}$ +2291°, $[\phi]_{261}$ −5509°; $[\phi]_{248}$ −5177°; $[\phi]_{226}$ −6262°. (Found: C, 60·0; H, 8·5; Br, 26·2. $C_{15}H_{25}OBr$ requires: C, 59·8; H, 8·3; Br, 26·5%).

*Lithium aluminium hydride reduction of* (−)-2α-*bromo*-4β,7β(H)-*eudesman*-3-*one* (VII)

A soln of VII (301 mg) in anhyd ether (15 ml) was added dropwise to a soln of LAH (60 mg) in anhyd ether (10 ml) at 0°. The reaction mixture was stirred at 25° for 45 min. Acetone was added dropwise at 0°, and the reaction mixture diluted with aqueous tartaric acid. Recovery in ether gave an oil which was adsorbed on alumina (25 g).

Ether/pet ether (1:3) eluted VIII (86 mg) which crystallized from pet ether as colourless prisms, m.p. 70–71°. Sublimation (100°/10 mm) gave colourless needles, m.p. 74–75°; $[\alpha]_D$ −6·7° (*c*, 4·2); IR spectrum in Nujol/HCB): $\nu_{max}$ 3322, 1460, 1374, 1053, 1021 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 6·34 (S); 7·10 (M); 9·05 (S); 9·09 (D); 9·14 (D); mass spectrum: parent ion *m/e* 224, base peak *m/e* 41. (Found: C, 80·3; H, 12·3. $C_{15}H_{28}O$ requires: C, 80·4; H, 12·5%).

Acetone eluted IX (46 mg) which crystallized from aqueous acetone as colourless needles, m.p. 129–130°; $[\alpha]_D$ −17° (*c*, 1·0); IR spectrum (in $CS_2$): $\nu_{max}$ 3612, 3584 $cm^{-1}$; mass spectrum: parent ion *m/e* 240, base peak *m/e* 41. (Found: C, 74·7; H, 11·3. $C_{15}H_{28}O_2$ requires: C, 75·0; H, 11·6%).

*Oxidation of* (−)-4β,7β(H)-*eudesman*-3β-*ol* (VIII)

(−)-4β,7β(*H*)-Eudesman-3β-ol (25 mg) in acetone at 0° was treated dropwise with 8N chromic acid.[25] Addition of water and recovery in ether gave an oil which was immediately treated with 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazone crystallized from EtOH/EtOAc as yellow needles, m.p. 225°, mixed m.p. 224°, with the 2,4-dinitrophenylhydrazone of (−)-4β,7β(*H*)-eudesman-3-one; Lit. records:[3] m.p. 221°.

(−)-4β,7β(H)-*Eudesman*-3β-*ol* (VIII)

A soln of (−)-4β,7β(*H*)-eudesman-3-one (222 mg) in anhyd ether (15 ml) was added dropwise to one of LAH (570 mg) in anhyd ether (10 ml). After stirring for 3 hr at 20°, acetone was added at 0° and aqueous tartaric acid at 20°. Recovery in ether gave an oil which was adsorbed on alumina (25 g). Ether/pet ether (1:3) eluted (−)-4β,7β(*H*)-eudesman-3β-ol which sublimed (100°/10 mm) to give fine colourless needles, m.p. 74°, mixed m.p. 74° with an authentic sample.

*Acetolysis of* (−)-2α-*bromo*-4β,7β(H)-*eudesman*-3-*one* (VII)

A soln of (−)-2α-bromo-4β,7β(*H*)-eudesman-3-one (307 mg) in anhyd AcOH (10 ml) containing freshly fused KOAc (2 g) was refluxed under $N_2$ for 4·5 hr. Dilution with water and recovery in ether gave an oil which was adsorbed on alumina (25 g).

Ether/pet ether (1:24) eluted X (53 mg) which crystallized from MeOH as colourless prisms, m.p. 107°; $[\alpha]_D$ +62 (*c*, 1·0); IR spectrum (in $CCl_4$): $\nu_{max}$ 1739, 1718, 1379, 1370, 1276, 1227 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 4·77 (Q); 7·94 (S); 8·76 (S); 9·04 (D); 9·11 (D); 9·14 (D); RD (in MeOH): $[\phi]_{400}$ +336°, $[\phi]_{300}$ +3388°, $[\phi]_{259}$ −4004°, $[\phi]_{239}$ −3304°, $[\phi]_{220}$ −3752°, $[\phi]_{213}$ −2590°; mass spectrum:

parent ion *m/e* 280, base peak *m/e* 238. (Found: C, 72·5; H, 10·2. $C_{17}H_{28}O_3$ requires: C, 72·8; H, 10·0%). Further elution with ether/pet ether (1:24) gave a mixture of X and XI (29 mg).

Ether/pet ether (1:19) eluted XI (38 mg) which crystallized from MeOH as colourless prisms, m.p. 92–93°; $[\alpha]_D$ +114·2° (*c*, 2·0); IR spectrum (in $CCl_4$): $\nu_{max}$ 1754, 1733, 1381, 1373, 1280, 1239, 1228 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 5·35 (D); 7·92 (S); 9·03 (S); 9·05 (D); 9·10 (D); RD (in MeOH): $[\phi]_{400}$ +882°, $[\phi]_{302}$ +4816°, $[\phi]_{262}$ −3305°, $[\phi]_{234}$ −1918°, $[\phi]_{217}$ −882°; mass spectrum: parent ion *m/e* 280, base peak *m/e* 95. (Found: C, 72·6; H, 9·75. $C_{17}H_{28}O_3$ requires: C, 72·8; H, 10·0%).

*Acetoxylation of* (−)-4β,7β(H)-*eudesman*-3-*one* (VI)

A soln of (−)-4β,7β(*H*)-eudesman-3-one (222 mg) and lead tetraacetate (497 mg) in benzene (10 ml) and MeOH (0·6 ml) containing $BF_3$–etherate (1·9 ml) was stirred at 25° for 2 hr. Dilution with water and recovery in ether gave an oil which was adsorbed on alumina (25 g).

Pet ether eluted (−)-2α-*methoxycarbonyl*-3β,6β(H)-A-*noreudesmane* (XII; 40 mg) as an oil, $n_D^{20}$ 1·4658; $[\alpha]_D$ −48·1° (*c*, 2·1); IR spectrum (in $CCl_4$): $\nu_{max}$ 1736, 1377, 1359, 1295, 1264, 1212 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 6·39 (S); 7·07 (Sex); 8·72 (S); 9·10 (D); 9·13 (D); 9·14 (D); mass spectrum: parent ion *m/e* 252, base peak *m/e* 166. (Found: C, 76·4; H, 10·7. $C_{16}H_{28}O_2$ requires: C, 76·2; H, 11·1%).

Ether/pet ether (3:97) eluted unchanged (−)-4β,7β(*H*)-eudesman-3-one (38 mg). Ether/pet ether (1:24) eluted (+)-2α-acetoxy-4β,7β(*H*)-eudesman-3-one (107 mg) and a mixture of (+)-2α-acetoxy-4β,7β(*H*)-eudesman-3-one and (+)-3β-acetoxy-4β,7β(*H*)-eudesman-2-one (15 mg). Ether/pet ether (1:19) eluted (+)-3β-acetoxy-4β,7β(*H*)-eudesman-2-one (54 mg).

*Isomerization of* (+)-2α-*acetoxy*-4β,7β(H)-*eudesman*-3-*one* (X)

(+)-2α-Acetoxy-4β,7β(*H*)-eudesman-3-one (90 mg) was adsorbed on basic alumina (10 g) and allowed to stand for 30 min. Ether/pet ether (1:24) eluted unchanged (+)-2α-acetoxy-4β,7β(*H*)-eudesman-3-one (35 mg). Ether/pet ether (1:19) eluted a mixture of (+)-2α-acetoxy-4β,7β(*H*)-eudesman-3-one and (+)-3β-acetoxy-4β,7β(*H*)-eudesman-2-one (21 mg). Further elution with ether/pet ether (1:19) gave (+)-3β-acetoxy-4β,7β(*H*)-eudesman-2-one (7 mg).

*Attempted isomerization of* (+)-3β-*acetoxy*-4β,7β(H)-*eudesman*-2-*one* (XI)

(+)-3β-Acetoxy-4β,7β(*H*)-eudesman-2-one (51 mg) was adsorbed on basic alumina (10 g) and allowed to stand for 30 min. Ether/pet ether (1:19) eluted (+)-3β-acetoxy-4β,7β(*H*)-eudesman-2-one (35·5 mg). No (+)-2α-acetoxy-4β,7β(*H*)-eudesman-3-one could be isolated.

(−)-2α-*Hydroxymethyl*-3β,6β(H)-A-*noreudesmane* (XIII)

A soln of (−)-2α-methoxycarbonyl-3β,6β(*H*)-A-norendesmane (420 mg) in anhyd ether (10 ml) was added dropwise to one of LAH (300 mg) in anhyd ether (10 ml) at 0°. After stirring for 3 hr at 25° acetone was added at 0° and aqueous tartaric acid at 25°. Recovery in ether gave an oil which was adsorbed on alumina (25 g). Ether/pet ether (1:9) eluted (−)-2α-*hydroxymethyl*-3β,6β(H)-A-*noreudesmane* (XIII; 297 mg) which sublimed (100°/10 mm) to give fine colourless needles, m.p. 63°; $[\alpha]_D$ −64·3° (*c*, 1·3); IR spectrum (in $CCl_4$): $\nu_{max}$ 3638, 3500, 1387, 1378, 1108, 1082, 1040 $cm^{-1}$. (Found: C, 80·6; H, 12·4. $C_{15}H_{28}O$ requires: C, 80·4; H, 12·5%).

(−)-4β,7β(H)-*Eudesman*-2α,3β-*diol* (IX)

Acetoxylation of (−)-4β,7β(*H*)-eudesman-3-one (222 mg) as above gave an oil which was dissolved in ether (15 ml) and treated with LAH (200 mg) in ether (10 ml) at 20°. Recovery in the usual way gave an oil which was adsorbed on alumina (25 g). Acetone eluted (−)-4β,7β(*H*)-eudesman-2α,3β-diol (35 mg) which crystallized from aqueous acetone as colourless needles, m.p. 129–130°. M.m.p. with previous sample, 129–130°. The IR spectra of the samples were identical.

p-*Tosylhydrazone of* (−)-4β,7β(H)-*eudesman*-3-*one* (VI)

The ketone VI (200 mg) and *p*-toluenesulphonylhydrazine (250 mg) were dissolved in MeOH (10 ml) and the mixture heated under reflux for 30 min. Removal of the solvent gave the p-*tosylhydrazone* of (−)-4β,7β(*H*)-eudesman-3-one, which crystallized from MeOH as colourless needles, m.p. 146—148° (dec); $[\alpha]_D$ +60° (*c*, 1·9); IR spectrum (in Nujol/HCB): $\nu_{max}$ 3225, 1610, 1387, 1366, 1190, 1170, 1098, 1009, 813 $cm^{-1}$. (Found: C, 67·8; H, 8·6; N, 7·2. $C_{22}H_{34}N_2O_2S$ requires: C, 67·8; H, 8·7; N, 7·2%).

(+)-3,3-*Ethylenedithio*-4β,7β(H)-*eudesman*-2α-*ol acetate* (XIV)

(+)-2α-Acetoxy-4β,7β(*H*)-eudesman-3-one (134 mg) dissolved in AcOH (0·2 ml) containing 1,2-ethanedithiol (0·2 ml) was treated with $BF_3$–etherate (0·2 ml) at 0°. After 1 hr the reaction mixture was adsorbed on alumina (10 g). Pet ether eluted (+)-3,3-*ethylenedithio*-4β,7β(H)-*eudesman*-2α-*ol acetate* as an oil which crystallized from MeOH as colourless prisms (143 mg), m.p. 123°, $[\alpha]_D$ +8·3° (*c*, 1·2); IR spectrum (in $CCl_4$): $\nu_{max}$ 1739, 1383, 1372, 1232 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 4·93 (Q); 6·84 (M); 8·00 (S); 8·87 (D); 8·98 (S); 9·11 (D); mass spectrum: parent ion *m/e* 356, base peak 296. (Found: C, 64·2; H, 8·9. $C_{19}H_{32}O_2S_2$ requires: C, 64·0; H, 9·0%).

(+)-3,3-*Ethylenedithio*-4β,7β(H)-*eudesman*-2α-*ol* (XV)

(+)-3,3-Ethylenedithio-4β,7β(*H*)-eudesman-2α-ol acetate (250 mg) was heated in methanolic KOH (30 ml, 2%) under reflux for 8 hr. Dilution with water and recovery in ether gave a yellow solid which was adsorbed on alumina (25 g). Ether/pet ether (3:17) eluted (+)-3,3-*ethylenedithio*-4β,7β(H)-*eudesman*-2α-*ol* (206 mg) which crystallized from MeOH as colourless needles, m.p. 126°, $[\alpha]_D$ +11·3° (*c*, 1·1); IR spectrum (in $CCl_4$): $\nu_{max}$ 3546, 1383, 1366, 1082, 1056, 1045 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 6·28 (Sep); 6·80 (M); 7·65 (D); 8·86 (D); 9·05 (S); 9·10 (D); mass spectrum: parent ion *m/e* 314, base peak *m/e* 271. (Found: C, 65·0; H, 9·4. $C_{17}H_{30}OS_2$ requires: C, 65·0; H, 9·5%).

(−)-4β,7β(H)-*Eudesman*-2α-*ol* (XVI)

A soln of (+)-3,3-ethylenedithio-4β,7β(*H*)-eudesman-2α-ol (250 mg) in acetone (40 ml) was heated under reflux for 3 hr over W-2 Raney Ni. Filtration and removal of the acetone *in vacuo* gave an oil which was adsorbed on alumina (25 g). Pet ether eluted an unidentified oil (44 mg); IR spectrum (natural film): $\nu_{max}$ 2941, 2857, 1642, 1453, 1437, 1372, 1366 $cm^{-1}$. Ether/pet ether (1:19) eluted impure (+)-4β,7β(H)-*eudesman*-2-*one* (35 mg). IR spectrum (natural film): $\nu_{max}$ 1709, 1377, 1364, 1272, 1235, 992 $cm^{-1}$. Ether/pet ether (1:4) eluted (−)-4β,7β(H)-*eudesman*-2α-*ol* (81 mg), which sublimed (100°/10 mm) to give fine colourless needles, m.p. 76°, $[\alpha]_D$ −38·2° (*c*, 1·2); IR spectrum (in $CCl_4$): $\nu_{max}$ 3663, 3509, 1381, 1370, 1081, 1049, 1036, 1026 $cm^{-1}$; mass spectrum: parent ion *m/e* 224, base peak *m/e* 109. (Found: C, 80·5; H, 12·2 $C_{15}H_{28}O$ requires: C, 80·4; H, 12·5%).

(+)-4β,7β(H)-*Eudesman*-2-*one* (II)

(−)-4β,7β(*H*)-Eudesman-2α-ol (140 mg) in acetone (2 ml) at 0° was treated dropwise with 8N chromic acid. Recovery in the usual way gave an oil which was adsorbed on alumina (25 g). Ether/pet ether (1:49) eluted (+)-4β,7β(*H*)-eudesman-2-one (92 mg) as an oil, $[\alpha]_D$ +35·2° (*c*, 1·05); IR spectrum (natural film): $\nu_{max}$ 1709, 1377, 1364, 1272, 1235, 992 $cm^{-1}$; RD (in MeOH): $[\phi]_{400}$ +293°, $[\phi]_{309}$ +2664°, $[\phi]_{266}$ −2842°, $[\phi]_{213}$ −1217°; mass spectrum: parent ion *m/e* 222, base peak *m/e* 95.

(−)-2,2-*Ethylenedithio*-4β,7β(H)-*eudesmane* (XVII)

(+)-4β,7β(*H*)-Eudesman-2-one (67 mg) dissolved in AcOH (0·2 ml) containing 1,2-ethanedithiol (0·2 ml) was treated with $BF_3$–etherate (0·2 ml) at 0°. After 1 hr the reaction mixture was adsorbed on alumina (10 g). Pet ether eluted (−)-2,2-*ethylenedithio*-4β,7β(H)-*eudesmane* (93 mg) as an oil which crystallized from MeOH as fine colourless needles, m.p. 90°, $[\alpha]_D$ −43° (*c*, 1·5); mass spectrum: parent ion *m/e* 298, base peak *m/e* 298. (Found: C, 68·4; H, 10·1. $C_{17}H_{30}S_2$ requires: C, 68·5; H, 10·1%).

(−)-3,3-*Ethylenedithio*-4β,7β(H)-*eudesmane* (XVIII)

(−)-4β,7β(*H*)-Eudesman-3-one (100 mg) dissolved in AcOH (0·25 ml) containing 1,2-ethanedithiol (0·25 ml) was treated with $BF_3$–etherate (0·25 ml) at 0°. After 1 hr the reaction mixture was adsorbed on alumina (10 g). Pet ether eluted (−)-3,3-*ethylenedithio*-4β,7β(H)-*eudesmane* as an oil which crystallized from MeOH as colourless needles (112 mg), m.p. 103°, $[\alpha]_D$ −8·1° (*c*, 3·1); NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 6·82 (M); 8·95 (D); 9·08 (S); 9·11 (D); mass spectrum: parent ion *m/e* 298, base peak *m/e* 132. (Found: C, 68·5; H, 10·0. $C_{17}H_{30}S_2$ requires: C, 68·5; H, 10·1%).

(−)-4β(H)-*Eudesman*-3-*one* (XIX)

(a) *From natural* (+)-α-*cyperone* (XX).[29] These transformations were carried out as described.[3] (−)-4β(*H*)-Eudesman-3-one was obtained as an oil; IR spectrum (natural film): $\nu_{max}$ 1709, 1385, 1377, 1368, 1346, 1307 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 8·93 (S); 8·98 (D); 9·10 (D). The oxime crystallized

from MeOH as colourless needles, m.p. 120–121°, $[\alpha]_D$ −115° (*c*, 1·0). (Found: C, 75·9; H, 11·2. Calc for $C_{15}H_{27}NO$: C, 75·9; H, 11·5%); Lit. records:[3] m.p. 118–119°, $[\alpha]_{5461}$ −126° (*c*, 1·7).

(b) *From the ketol* (V) *via* (+)-β-*cyperone* (XXII). These transformations were carried out as described.[3] (−)-4β(*H*)-Eudesman-3-one was obtained as an oil; IR spectrum (natural film): $\nu_{max}$ 1709, 1377, 1366 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 8·93 (S); 8·99 (D); 9·00 (D), 9·10 (S). The oxime crystallized from MeOH as colourless needles, m.p. 119–120°, $[\alpha]_D$ −90° (*c*, 0·5). Lit. records[3]: m.p. 119–120°, $[\alpha]_{5461}$ −116° (*c*, 1·1).

(c) *From the ketol* (V) *via* (+)-*epi*-α-*cyperone* (XXI). These transformations were carried out as described.[3] (−)-4β(*H*)-Eudesman-3-one was obtained as an oil. The IR and NMR spectra of this sample were identical to those of the sample prepared *via* the reduction of natural (+)-α-cyperone. The oxime crystallized from MeOH as colourless needles, m.p. 123–124, $[\alpha]_D$ −117° (*c*, 1·0), mixed m.p. 122–123° with the oxime prepared *via* the reduction of natural (+)-α-cyperone. The NMR spectra of the two oximes were superimposable. (Found: C, 75·8; H, 11·2. Calc. for $C_{15}H_{27}NO$: C, 75·9; H, 11·5%). Lit. records[3]: m.p. 118–119°, $[\alpha]_{5461}$ −130° (*c*, 3·1).

*Isomerization of* (+)-4β,7β(H)-*Eudesm*-11-*en*-3-*one* (XXIV)

(+)-4β,7β(*H*)-Eudesm-11-en-3-one (238 mg) in EtOH (10 ml) containing 1 drop of AcOH was heated under reflux for 114 hr over Pd-C (255 mg). Filtration and removal of the ethanol *in vacuo* gave an oil which was adsorbed on alumina (25 g). Pet ether eluted a mixture of XXV, XXVI, and XXVII as an oil (219 mg); IR spectrum (natural film): $\nu_{max}$ 1709, 1377, 1346, 1142, 843, 809, 775, 731 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 4·66 (M); 5·36 (M); 8·35 (S); 8·84 (S); 9·00 (D); 9·05 (D).

*Hydrolysis of* (−)-4β(*H*)-*eudesman*-3-*one* oxime

The oxime (m.p. 122°, $[\alpha]_D$ −116°, 1·25 g) in MeOH (55 ml), water (25 ml) and pet ether (20 ml) was refluxed for 24 hr with oxalic acid (3 g) and aqueous formaldehyde (15 ml, 40%). Addition of water and extraction with pet ether gave (−)-4β(*H*)-eudesman-3-one (907 mg) as an oil; IR spectrum (natural film): $\nu_{max}$ 1709, 1385, 1377, 1368, 1346, 1307 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 8·93 (S); 8·98 (D); 9·10 (D). RD (in MeOH): $[\phi]_{400}$ 0°, $[\phi]_{306}$ +1887°, $[\phi]_{265}$ −3312°, $[\phi]_{235}$ −2819°, $[\phi]_{217}$ −3418°; mass spectrum: parent ion *m/e* 222, base peak *m/e* 69.

2α-*Bromo*-4β(*H*)-*eudesman*-3-*one* (XXIX).

(−)-4β(*H*)-Eudesman-3-one (141 mg) in AcOH (10 ml) was treated with 1 drop of a saturated solution of HBr in AcOH and then dropwise with a soln of $Br_2$ (119 mg) and anhyd NaOAc (60 mg) in AcOH (7 ml). Recovery in the usual way gave an oil which was adsorbed on alumina (20 g). Ether/pet ether (1:49) eluted 2α-*bromo*-4β(*H*)-*eudesman*-3-*one* as an oil (73 mg); IR spectrum (natural film): $\nu_{max}$ 1724, 1449, 1379, 1366, 1299, 1170 $cm^{-1}$. (Found: C, 60·1; H, 8·3. $C_{15}H_{25}OBr$ requires: C, 59·8; H, 8·3%). The instability of the compound prevented any further data being recorded.

*Acetoxylation of* (−)-4β(*H*)-*eudesman*-3-*one* (XIX)

A soln of (−)-4β(*H*)-eudesman-3-one (227 mg) and lead tetra-acetate (498 mg) in benzene (10 ml) and MeOH (0·6 ml) containing $BF_3$-etherate (1·9 ml) was stirred at 20° for 3 hr. Recovery in the usual way gave an oil which was adsorbed on alumina (25 g). Pet. ether eluted (−)-2α-*methoxycarbonyl*-3β(H)-A-*nor*-*eudesmane* (XXXII, 60 mg), as an oil, $n_D^{20}$ 1·4739, $[\alpha]_D$ −30·2° (*c*, 1·2); IR spectrum (natural film): $\nu_{max}$ 1736, 1381, 1362, 1267, 1220, 1192, 1163 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 6·41 (S); 7·04 (Sex); 9·07 (S); 9·09 (D); 9·12 (D); 9·18 (D); mass spectrum: parent ion *m/e* 252, base peak *m/e* 166. (Found: C, 76·5; H, 11·0. $C_{16}H_{28}O_2$ requires: C, 76·2; H, 11·1%).

Ether/pet ether (1:49) eluted unchanged (−)-4β(*H*)-eudesman-3-one (16 mg). Ether/pet. ether (1:24) eluted (+)-2α-*acetoxy*-4β(H)-*eudesman*-3-*one* (XXX, 80 mg), m.p. 52–53°, $[\alpha]_D$ +92·9° (*c*, 1·13); IR spectrum (in $CCl_4$): $\nu_{max}$ 1751, 1733, 1379, 1370, 1292, 1280, 1229 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 4·77 (Q); 7·94 (S); 8·81 (S); 9·01 (D); 9·09 (D); RD (in MeOH): $[\phi]_{400}$ +308°, $[\phi]_{305}$ +3752°, $[\phi]_{264}$ −4256°, $[\phi]_{222}$ −3472°; mass spectrum: parent ion *m/e* 280, base peak *m/e* 238. (Found: C, 73·1; H, 10·0. $C_{17}H_{28}O_3$ requires: C, 72·8; H, 10·0%).

Ether/pet ether (1:9) eluted (+)-3β-*acetoxy*-4β(H)-*eudesman*-2-*one* (XXXI, 25 mg), as an oil, $[\alpha]_D$ +108·9° (*c*, 1·1); IR spectrum (natural film): $\nu_{max}$ 1751, 1724, 1379, 1366, 1279, 1238, 1221 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 5·30 (D); 7·91 (S); 8·98 (D); 9·03 (S); 9·20 (D).

(+)-3,3-*Ethylenedithio*-4β(H)-*eudesman*-2α-*ol Acetate* (XXXIII).

(+)-2α-Acetoxy-4β(*H*)-eudesman-3-one (360 mg) dissolved in AcOH (0·25 ml) containing 1,2-ethanedithiol (0·25 ml) was treated with $BF_3$-etherate (0·25 ml) at 0°. After 1 hr the reaction mixture was adsorbed on alumina (10 g). Pet ether eluted (+)-3,3-*ethylenedithio*-4β(H)-*eudesman*-2α-*ol acetate* which crystallized from MeOH as colourless prisms (414 mg), m.p. 123°, $[\alpha]_D$ +30·1° (*c*, 1·33); IR spectrum (in $CCl_4$): $\nu_{max}$ 1743, 1387, 1370, 1282, 1233 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 4·91 (Q); 6·83 (M); 8·02 (S); 8·87 (D); 9·06 (S); 9·11 (D); mass spectrum: parent ion *m/e* 356, base peak *m/e* 43. (Found: C, 63·9; H, 8·8. $C_{19}H_{32}O_2S_2$ requires: C, 64·0; H, 9·0%).

(+)-3,3-*Ethylenedithio*-4β(H)-*eudesman*-2α-*ol* (XXIV).

(+)-3,3-Ethylenedithio-4β(*H*)-eudesman-2α-ol acetate (480 mg) was heated in methanolic KOH (60 ml, 2%) under reflux for 8 hr. Dilution with water and recovery in ether gave a yellow solid which was adsorbed on alumina (25 g). Ether/pet ether (1:9) eluted (+)-3,3-*ethylenedithio*-4β(H)-*eudesman*-2α-*ol* (449 mg) which crystallized from aqueous MeOH as colourless needles, m.p. 82·5–83°, $[\alpha]_D$ +19·4° (*c*, 1·1); IR spectrum (in $CCl_4$): $\nu_{max}$ 3515, 1389, 1377, 1095, 1070, 1052 $cm^{-1}$; NMR spectrum (in $CCl_4$, 1% $SiMe_4$): τ 6·24 (Q); 6·82 (M); 7·60 (S); 8·86 (D); 9·13 (S); 9·14 (D); mass spectrum: parent ion *m/e* 314, base peak *m/e* 271. (Found: C, 65·1; H, 9·5. $C_{17}H_{30}OS_2$ requires: C, 65·0; H, 9·5%).

4β(H)-*Eudesman*-2α-*ol* (XXXV).

A soln of (+)-3,3-ethylenedithio-4β(*H*)-eudesman-2α-ol (440 mg) in acetone (40 ml) was heated under reflux for 3 hr over W-2 Raney Ni Filtration and removal of the acetone *in vacuo* gave an oil which was adsorbed on alumina (25 g). Pet. ether eluted an unidentified oil (42 mg); IR spectrum (natural film): $\nu_{max}$ 2941, 1642, 1453, 1437, 1372, 1366 $cm^{-1}$.

Ether/pet ether (1:19) eluted impure (+)-4β(H)-*eudesman*-2-*one* (65 mg); IR spectrum (natural film): $\nu_{max}$ 1709, 1372, 1362, 1274, 1235 $cm^{-1}$.

Ether/pet ether (1:4) eluted 4β(H)-*eudesman*-2α-*ol* (135 mg) as an oil; IR spectrum (natural film): $\nu_{max}$ 3344, 1370, 1357, 1136, 1071, 1025 $cm^{-1}$; mass spectrum: parent ion *m/e* 224, base peak *m/e* 165.

(+)-4β(H)-*Eudesman*-2-*one* (III).

4β(*H*)-Eudesman-2α-ol (110 mg) in acetone (2 ml) at 0° was treated dropwise with 8N chromic acid. Recovery in the usual way gave an oil which was adsorbed on alumina (25 g). Ether/pet ether (1:49) eluted (+)-4β(*H*)-eudesman-2-one (96 mg) as an oil, $[\alpha]_D$ +60·8° (*c*, 1·15); IR spectrum (natural film): $\nu_{max}$ 1709, 1372, 1362, 1274, 1235 $cm^{-1}$; RD (in MeOH): $[\phi]_{400}$ +179°, $[\phi]_{309}$ +2253°, $[\phi]_{268}$ −2375°, $[\phi]_{213}$ −590°; mass spectrum: parent ion *m/e* 222, base peak *m/e* 95.

*Acknowledgements*—One of us (D.L.R.) gratefully acknowledges an S.R.C. Research Studentship. We are grateful to E. J. Bush and Co. Ltd. for a gift of (+)-carvone.

## REFERENCES

[1] W. Herz, R. B. Mitra, K. Rabindran and N. Viswanathan, *J. Org. Chem.* **27**, 4041 (1962).
[2] [a] F. J. McQuillin, *J. Chem. Soc.* 528 (1955);
[b] T. G. Halsall, D. W. Theobald and K. B. Walshaw *Ibid.* 1029 (1964).
[3] R. Howe and F. J. McQuillin, *Ibid.* 2670 (1956); 1194 (1958).
[4] J. A. Marshall, N. Cohen and K. R. Arenson, *J. Org. Chem.* **30**, 762 (1965).
[5] E. J. Corey, *J. Am. Chem. Soc.* **75**, 4832 (1953).
[6] C. W. Shoppee, G. A. R. Johnston and R. E. Lack, *J. Chem. Soc.* 3604 (1962).
[7] R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, *J. Am. Chem. Soc.* **74**, 2828 (1952); E. G. Cummins and J. E. Page, *J. Chem. Soc.* 3847 (1957).
[8] A. Nickon, M. A. Castle, R. Harada, C. E. Berkoff and R. O. Williams, *J. Am. Chem. Soc.* **85**, 2185 (1963).
[9] R. J. Abraham and J. S. E. Holker, *J. Chem. Soc.* 806 (1963). J-M. Lehn and G. Ourisson, *Bull. Soc. chim. Fr.* 1113 (1963).
[10] M. Karplus, *J. Chem. Phys.* **30**, 11 (1959).
[11] C. Djerassi, *Optical Rotatory Dispersion—Applications to Organic Chemistry* p. 116. McGraw-Hill, New York (1960).
[12] L. P. Kuhn, *J. Am. Chem. Soc.* **76**, 4323 (1954); **74**, 2492 (1952).
[13] H. B. Henbest and T. I. Wrigley, *J. Chem. Soc.* 4596 (1957).

[14] K. L. Williamson and W. S. Johnson, *J. Am. Chem. Soc.* **83**, 4623 (1961).
[15] A. Lablache-Combier, B. Lacoume and J. Levisalles, *Bull. Soc. Chim. Fr.* 897 (1966).
[16] H. B. Henbest, D. N. Jones and G. P. Slater, *J. Chem. Soc.* 4472 (1961); J. D. Cocker, H. B. Henbest, G. H. Phillips, G. P. Slater and D. A. Thomas, *Ibid.* 6 (1965).
[17] H. B. Henbest, D. N. Jones and G. P. Slater, *Ibid.* C, 756 (1967).
[18] L. Caglioti and M. Magi, *Tetrahedron* **19**, 1127 (1963); L. Caglioti and M. Grasselli, *Chem. & Ind.* 153 (1964); L. Caglioti, *Tetrahedron* **22**, 487 (1966).
[19] R. S. Rosenfeld and T. F. Gallagher, *J. Am. Chem. Soc.* **77**, 4367 (1955).
[20] L. F. Fieser and M. A. Romero, *Ibid.* **75**, 4716 (1953).
[21] P. N. Rao and H. R. Goldberg, *Tetrahedron* **18**, 1251 (1962).
[22] J. Fishman, *Chem. & Ind.* 1467 (1962).
[23] R. Mozingo, *Organic Syntheses*, Coll Vol. 3; p. 181.
[24] S. Pietra and G. Traverso, *Gazz. Chim. Ital.* **81**, 687 (1951).
[25] A. Bowers, T. G. Halsall, E. R. H. Jones and A. J. Lemin, *J. Chem. Soc.* 2548 (1953).
[26] H. Budzikiewicz, C. Djerassi and D. H. Williams, *Structure Elucidation of Natural Products by Mass Spectroscopy* Vol. 2; p. 74. Holden Day, San Francisco (1964).
[27] W. D. Moffitt, A. Moscowitz, R. B. Woodward, W. Klyne and C. Djerassi, *J. Am. Chem. Soc.* **83**, 4013 (1961).
[28] C. Djerassi, O. Halpern, V. Halpern, O. Schindler and C. Tamm, *Helv. Chim. Acta.* **41**, 250 (1958).
[29] Kindly supplied by Dr. S. Dev.