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REARRANGEMENT OF 4,5-EPOXY-EUDESMANES WITH BORON TRIFLUORIDE*

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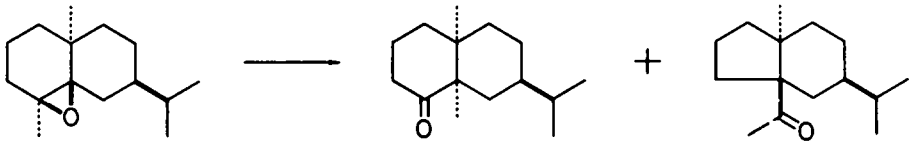
Abstract—Three epoxides (IX, XIX and XX) prepared from the eudesm-4-enes (VIII and XVIII) on treatment with BF_3-etherate have been found to undergo skeletal rearrangement resulting in the formation of a number of ketones; i.e. 5-*epi*faurinan-4-one (X), 1(*R*)-isopropyl-3-(1'-methyl-5-oxohexylidene)cyclopentane (XI) and 1(*S*),7(*S*)-dimethyl-4(*R*)-isopropyl-bicyclo[5.3.0]decan-6-one (XII) from 4α,5α-epoxy-10-*epi*eudesmane (IX), 1(*R*),7(*S*)-dimethyl-4(*R*)-isopropyl-bicyclo[5.3.0]decan-6-one (XXI) from 4α,5α-epoxy-eudesmane (XIX), and the unsaturated methyl ketone (XI) from 4β,5β-epoxy-eudesmane (XX).

RECENTLY we isolated from various kinds of Japanese valerian the rearranged sesquiterpenoids, valeranone and faurinone, and elucidated their stereostructures I and II respectively.[1,2] From the biogenetic point of view, the co-occurrence of the rearranged isoprenoids (I and II) in the same plants suggests that both ketones are derived from a common precursor, 4β,5β-epoxy-10-*epi*eudesmane (III) or its equivalent, by pinacolic rearrangement. In the hope of synthesizing valeranone (I) and/or faurinone (II) by chemical procedures from the epoxide III, the present work was initiated.



III I II

On the other hand, we observed during our work on the synthesis of cyperolone that the 4,5-epoxy-eudesmanes with oxygen functions at C-3 rearranged with BF_3 to a variety of ketonic products.[3] Since a polar substituent in the vicinity of the epoxide group is known to alter the course of the reaction, the behaviour of the 4,5-epoxy-eudesmanes, with no substituent at C-3, with BF_3 was the second object of our interest.

In the present work, the isomerization reaction was applied to epoxides prepared from 10-*epi*eudesm-4-ene (VIII) and eudesm-4-ene (XVIII) and in every case the oxide rearrangement took place forming a number of products in which the ketonic components were examined.

Partial hydrogenation of 10-*epi*eudesm-11-en-3-on-5α-ol (IV)[4] gave 10-*epi*-eudesman-3-on-5α-ol (V) which was dehydrated by hydrochloric acid to yield 10-*epi*eudesm-4-en-3-one (VI). 10-*epi*Eudesm-4-ene (VIII) was obtained from the enone

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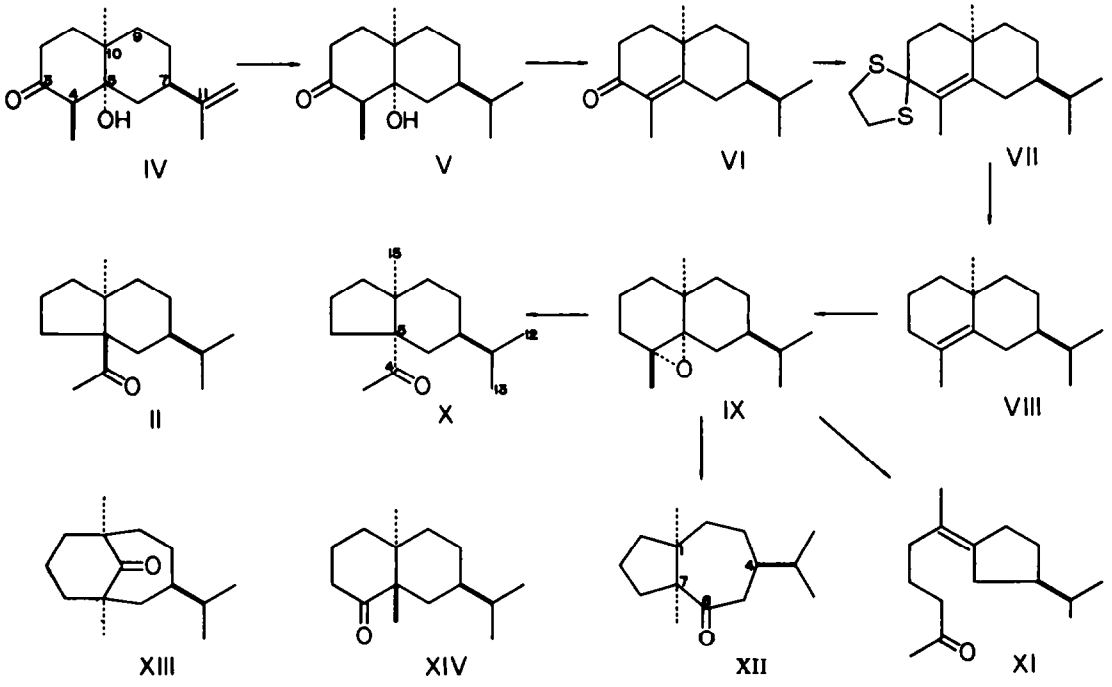
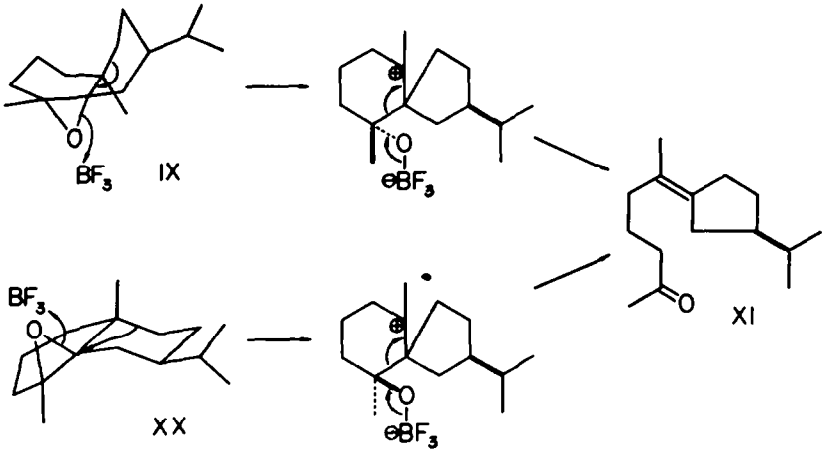
(VI) *via* the ethylene thioketal (VII) and a subsequent desulfurization with Raney nickel. The epoxidation of this olefin (VIII) with perbenzoic acid afforded a single epoxide (IX). The configuration of the epoxide ring cannot be established by its physico-chemical data, since no data of its counterpart are available. However, the stereochemistry of its rearranged products which follow along with the mechanistic considerations of the rearrangement reactions indicate that the epoxide ring is α-oriented. Therefore, it is evident that peracid attacks the olefin (VIII) almost exclusively from the undesirable α-face.



The rearrangement reaction was carried out by the addition of BF_3-etherate to a solution of the epoxide (IX) in benzene. At room temperature, the reaction gave a mixture (chromatography) of three ketonic products. The first and the least polar product has the composition $C_{15}H_{26}O$. The IR and NMR spectra indicate the presence of an acetyl (1699 cm^{-1}, 1·96 ppm), a tertiary Me (0·88 ppm) and an isopropyl group (0·84 ppm). Since there is no other centre of unsaturation, it is concluded to be bicyclic. The above evidence suggests that the first product may have either stereostructure X or II. The decision in favour of X is made by the following observations. In a previous paper,[2] we discussed the conformation of ketones of this type and concluded that the CD curves of the ketones X and II would show a negative and a positive Cotton effect, respectively, and that in both ketones X and II the solvent-induced shifts ($\Delta^{CHCl_3}_{C_6H_6}$) for the C-15 Me protons would be negative and positive, respectively, and those for the C-12 and C-13 Me protons would be positive and nearly zero, and negative and negative, respectively. In fact, the ketone II, faurinone, showed the spectral properties consistent with the above prediction,[2] but is not identical with

the product in question. On the other hand, the first product showed a negative Cotton effect in the CD curve and exhibited a negative solvent shift for the C-15 protons ($\Delta_{C_6H_6}^{CHCl_3}$ −0·10 ppm) and small but positive solvent shifts for the C-12 and C-13 protons (both $\Delta_{C_6H_6}^{CHCl_3}$ +0·03 ppm), confirming the structure X. The second product analysed for $C_{15}H_{26}O$ (M^+ at *m/e* 222) and is unsaturated as shown by a positive tetranitromethane test. The NMR spectrum indicates that the isopropyl group in the original epoxide (IX) is still retained in the product. However, the absence of the signals, in the spectrum of the starting material (IX), associated with the tertiary Me and the tertiary Me on carbon bearing epoxide oxygen, and instead the presence of a 3-proton peak at 1·57 ppm assigned to a vinyl Me group and a 3-proton peak at 2·02 ppm attributed to an acetyl Me group demonstrate that the environment of these Me groups has been changed during the rearrangement. The presence of the acetyl group was further confirmed by IR bands at 1718 and 1358 cm^{-1}. Since no vinyl proton signals are visible, the ethylenic linkage is tetrasubstituted. The vinyl Me signal is fairly broadened conceivably due to long-range couplings to methylene protons adjacent to the ethylenic bond. These observations point to the structure XI for the second product. The transformation of the epoxide IX into the unsaturated methyl ketone XI can be rationalized by a possible mechanism outlined in Chart 1. The third

CHART 1



and the most polar product has the molecular formula $C_{15}H_{26}O$. The NMR spectrum reveals the presence of two tertiary Me's and two secondary Me's which must be involved in an isopropyl group. The IR spectrum indicates that a carbonyl group in a 6- or larger-membered ring (1708 cm^{-1}) has been formed. Therefore, the rearrangement has converted the epoxide ring bearing the Me group into the carbonyl and the tertiary Me group. Three possible structures XII, XIII and XIV are consistent with the above spectral properties. The facts that a methylene grouping is adjacent to the carbonyl (2H multiplet around 2·5 ppm) and that the solvent-induced shifts for the two tertiary Me groups are not equal ($\Delta_{C_6H_6}^{CHCl_3}$ +0·27 and +0·08 ppm), exclude the possible structure XIII for the third product. Therefore, two formulas XII and XIV remain. The CD curve of the third product shows a negative Cotton effect. However,

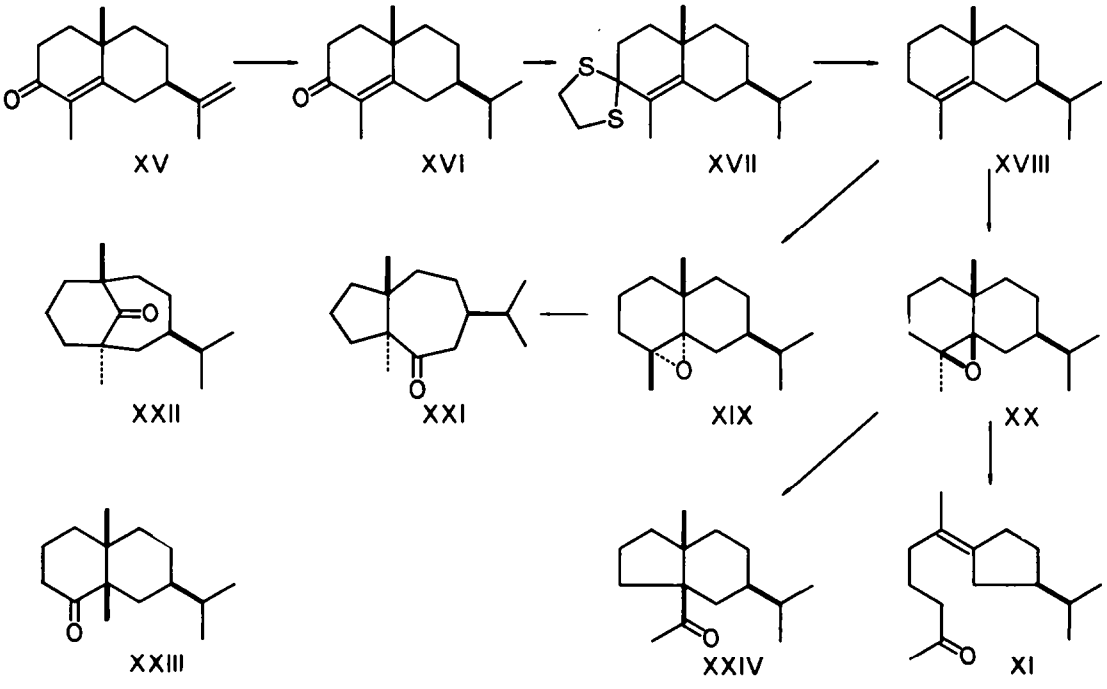
this cannot serve for the selection between the two possible structures XII and XIV, since the substance XIV is expected to give a negative Cotton curve, but the ring system of the substance XII is considered to be flexible, preventing a definite prediction of the conformation and consequently the sign of the Cotton effect. In the substance XIV, the isopropyl-carrying ring is very likely in a twist form so as to make the isopropyl group quasi-equatorial. In this conformation, one of two Me's of the isopropyl group lies in front of the reference plane, the solvent-induced shift of the Me signal being expected to be negative. On the other hand, in the substance XII, two Me's of the isopropyl are probably situated behind the reference plane. Experimentally, the solvent shifts of these two Me's are shown to be both positive ($\Delta^{CHCl_3}_{C_6H_6}$ +0·05 and +0·08 ppm), a fact which demonstrates that the product is represented by formula XII.

Since the epoxidation of the olefin VIII gave only the unfavourable α-epoxide (IX) but not the desired β-epoxide (III), synthesis of valeranone (I) and faurinone (II) could not be achieved.

Next, the reactions of the 4,5-epoxy-eudesmanes with BF_3 were examined.

α-Cyperone (XV) when hydrogenated over Adams' catalyst in methanol underwent selective saturation at the vinylidene group to yield dihydro-α-cyperone (XVI) which retained the tetrasubstituted double bond, as shown by an NMR signal at 1·72 ppm due to a vinyl Me. Since removal of the carbonyl group from the enone (XVI) by the Huang-Minlon procedure resulted in the concomitant migration of the ethylenic linkage to give a mixture of eudesm-4-ene and eudesm-3-ene, the enone (XVI) was reduced *via* the ethylene thioketal (XVII) and a subsequent desulphurization with Raney nickel yielding eudesm-4-ene (XVIII). Epoxidation of the hydrocarbon (XVIII) with perbenzoic acid gave a mixture of the unstable 4α,5α-epoxide (XIX) and 4β,5β-epoxide (XX) in approximately 1:1 ratio. The configuration of the epoxy rings of both oxides, separated by column chromatography, were confirmed by comparison of their molecular rotations ($[M]_D$ +141 for XIX and $[M]_D$ +26 for XX) with those reported for the epimeric 4-methyl-4,5-epoxy-cholestanes and 3-acetoxy-4-methyl-4,5-epoxy-cholestanes; molecular rotations of 4α,5α-epoxides being more dextrorotatory than those of the corresponding 4β,5β-epoxides.[5,6]

The rearrangement reactions were carried out in similar manners described above. The rearrangement of 4α,5α-epoxy-eudesmane (XIX) was straightforward. Chromatography of the reaction mixture led to the isolation of 1(*R*),7(*S*)-dimethyl-4(*R*)-isopropyl-bicyclo[5.3.0]decan-6-one (XXI) as the only ketonic product, whose structure was deduced by the following evidence. The IR spectrum shows the presence of a carbonyl in a 6- or larger-membered ring (1694 cm^{-1}). In the NMR spectrum, two Me singlets (0·91 and 1·07 ppm) and two Me doublets (0·88 ppm) are visible. These spectral characteristics point to three possible structures XXI, XXII and XXIII for the product. The presence of a methylene group (2H multiplet around τ 5 ppm) precludes the possibility XXII. In the compound XXI, two Me's of the isopropyl group are situated behind the carbonyl, while in the compound XXIII, both Me's of the isopropyl lie in front of the reference plane. Experimentally, the solvent-induced shifts of these two Me's are found to be both positive ($\Delta^{CHCl_3}_{C_6C_6}$ +0·08 and +0·11 ppm), indicating that the product possesses the structure XXI. The ORD and CD curves of the product show a positive Cotton effect which, however, could not be a difinite evidence for distinction of the two structures XXI and XXIII, since no decisive



prediction from the possible octant diagrams can be drawn. However, the relative change of the CD of the ketone XXI by going from low to high temperature ($-180° \rightarrow +20°$) is -3%, while that of the ketone XII ($-158° \rightarrow +20°$) is -29%, the latter being much greater than for the former. These phenomena may be in accordance with the present conclusion that the ketone XXI possesses a *trans*-fused ring system which is more rigid than its *cis*-congener (XII), and that the ketone XII consists of a *cis*-fused ring system which necessarily has a higher order of freedom than its *trans*-analogue (XXI).

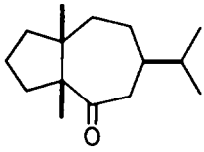
The behaviour of 4β,5β-epoxy-eudesmane (XX) with BF_3 was again unusual. The monocyclic unsaturated methyl ketone XI was identified as a main constituent of the ketonic fraction obtained by chromatography of the crude reaction product. Although the bicyclic acetyl derivative, cyperan-4-one (XXIV), could not be isolated pure, its presence of the reaction mixture was suggested from the NMR spectrum of a fraction which exhibited all the features of the ketone XXIV, with additional peaks, especially singlet at 2·10 ppm due to the acetyl Me group. Formation of the same rearrangement product XI from the two epoxides (IX and XX of different skeletons) can reasonably be explained by the following mechanisms. Thus, it is apparent from inspection of Dreiding models that both epoxides IX and XX have the common conformational features, i.e. the C-9:C-10 bonds being situated in the antiparallel positions to the O:C-5 bonds. Therefore, concerted migration of the C-9:C-10 bondings upon C-5 favours with the initial rupture of the O:C-5 bonds, as shown in Chart 1, yielding the same ultimate product XI.

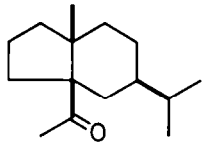
These transformations of the epoxides IX and XX to the methyl ketone XI clearly indicate that formation of the electron-deficient centre at C-5 initially leads to the

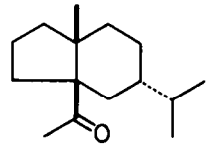
genesis of a β-vetivane type skeleton. In these cases, however, the retention of the oxygen functions at C-4 facilitates further cleavage of the C-4:C-5 bonds. Therefore, stereochemically favourable generation of the carbonium ion at C-5 in the eudesmane skeleton having no oxygen function at C-4, e.g. elimination of the C-5β OH group, will certainly cause a similar rearrangement giving a β-vetivane type skeleton but prevent further fission of the C-4:C-5 bond. This process may serve for synthesis of certain sesquiterpenoids containing spiro[4.5]decane ring system.[7]

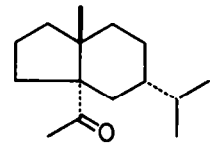
It was thus found that 4,5-epoxy-eudesmanes react with BF_3 in different ways from 3-oxygenated 4,5-epoxy-eudesmanes.

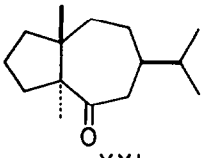
Immediately before the submission of the present paper, Mehta *et al.*[8] announced a similar rearrangement of the 4,5-epoxy-eudesmanes with BF_3- etherate in toluene solution at $-15°$ for 30 min. To our surprise, however, all the structures assigned to the products obtained from the three rearrangement reactions do not agree with those presently deduced by us for our products. We will not discuss the discrepancy in detail here, since it is readily solved by the evidence described in our previous papers[2,3] and this paper. In conclusion, the products, for which they allege the structures XXV, XXVI, XXVII and XXVIII, appear to be XXI, XI, XXIX (antipodal XI) and XXVII (antipodal X), respectively. Consequently, some of the mechanisms which they postulate are irrelevant.

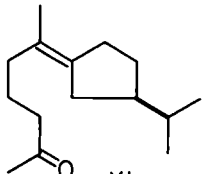

XXV

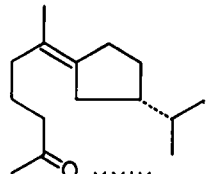

XXVI

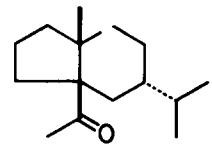

XXVII


XXVIII


XXI


XI


XXIX


XXVII

EXPERIMENTAL

M.ps are uncorrected. Specific rotations were measured in $CHCl_3$ soln. NMR spectra were determined at 60 MHz. Chemical shifts are given in ppm from TMS as internal reference and coupling constants (J) in Hz unit. Abbreviations: s = singlet, d = doublet, m = multiplet, and br = broad.

Hydrogenation of 10-epi*eudesm*-11-*en*-3-*on*-5α-*ol over Adams' catalyst in methanol.* Compound IV (5·25 g) in MeOH (50 ml) was hydrogenated over PtO_2 (0·25 g). After the uptake of 1 mole of H_2, the catalyst was filtered off and the solvent distilled off. Distillation under reduced press yielded V as a colourless oil (5·13 g), $[\alpha]_D$ +101·5° (c = 5·20), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3620, 3530 (OH), 1710 (cyclohexanone), NMR (CCl_4): 6H d at 0·83 (J = 5, $(CH_3)_2CH$—), 3H d at 0·95 (J = 6, CH_3—CH<), 3H s at 1·17 (CH_3—C<). (Found: C, 75·75; H, 10·78. $C_{15}H_{26}O_2$ requires: C, 75·58; H, 10·29%).

Dehydration of 10-epi*eudesman*-3-*on*-5α-*ol with hydrochloric acid.* The ketol V (5·12 g) in conc HCl (9 ml) and EtOH (20 ml) was left at room temp for 4 days. Upon isolation in the customary way, the product was distilled under reduced press to give VI as a colourless oil (4·47 g), $[\alpha]_D$ −145·0° (c = 9·35), UV λ_{max}^{EtOH} mμ

(log ε): 252 (4·28), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1665 (cyclohexenone), NMR (CCl_4): two 3H d at 0·86, 0·94 (J = 5, $(C\underline{H}_3)_2CH$—), 3H s at 1·22 ($C\underline{H}_3$—C<), 3H d at 1·69 (J = 1, $C\underline{H}_3$—C=C).

Thioketalization of 10-epi*eudesm-4-en-3-one.* The enone VI (4·10 g) was treated with $HSCH_2CH_2SH$ (2·5 g) and $BF_3 \cdot Et_2O$ (2 ml) at room temp for 1 day. Ether extraction followed by crystallization from EtOH yielded VII as colourless prisms (4·10 g), m.p. 90–91°, $[\alpha]_D$ −111·2° (c = 9·60), NMR (CCl_4): two 3H d at 0·83, 0·93 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 1·09 ($C\underline{H}_3$—C<), 3H s at 1·85 ($C\underline{H}_3$—C=C), 4H m at ~3·2 (—S—$(C\underline{H}_2)_2$—S—). (Found: C, 68·09; H, 9·25. $C_{17}H_{28}S_2$ requires: C, 68·24; H, 9·46%).

Reduction of 10-epi*eudesm-4-en-3-one ethylene thioketal with Raney nickel.* The thioketal VII (3·98 g) in EtOH (400 ml) was refluxed with Raney Ni (30 g) for 24 hr. The mixture furnished VIII as a colourless oil (1·75 g), NMR (CCl_4): two 3H d at 0·82, 0·90 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 1·04 ($C\underline{H}_3$—C<), 3H s at 1·58 ($C\underline{H}_3$—C=C).

Epoxidation of 10-epi*eudesm-4-ene with perbenzoic acid.* The hydrocarbon VIII (1·52 g) was treated with BzOOH (2·0 g) in $CHCl_3$ (57 ml) at room temp for 1 day. After isolation the product was distilled under reduced press to give IX as a colourless oil (1·71 g), $[\alpha]_D$ −28·5° (c = 6·17), NMR (CCl_4): two 3H d at 0·88, 0·92 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 1·01 ($C\underline{H}_3$—C<), 3H s at 1·21 ($C\underline{H}_3$—C(O)C<). (Found: C, 81·38; H, 11·47. $C_{15}H_{16}O$ requires: C, 81·02; H, 11·79%).

Rearrangement of 4α,5α-*epoxy*-10-epi*eudesmane with boron trifluoride etherate.* The epoxide IX (70 mg) in benzene (2 ml) was treated with BF_3–Et_2O (0·2 ml) at room temp. After 3 min, water was added and the product was extracted by use of ether. Chromatography on alumina followed by rechromatography over silica gel furnished the following products.

Compound X as a colourless oil, MS m/e: 222 (M^+), CD (c = 0·0909, MeOH): $[\theta]_{285}^{24°}$ −480, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1699 (acetyl), NMR (CCl_4): 6H d at 0·83 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 0·87 ($C\underline{H}_3$—C<), 3H s at 1·96 ($C\underline{H}_3$—CO—), NMR ($CHCl_3$): 6H d at 0·81 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 0·90 ($C\underline{H}_3$—C<), 3H s at 2·00 ($C\underline{H}_3$—CO—), NMR (C_6H_6): 6H d at 0·78 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 1·00 ($C\underline{H}_3$—C<), 3H s at 1·77 ($C\underline{H}_3$—CO—).

Compound XI as a colourless oil, MS m/e: 222 (M^+), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1718, 1358 (acetyl), NMR (CCl_4): 6H d at 0·89 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 1·57 ($C\underline{H}_3$—C=C), 3H s at 2·02 ($C\underline{H}_3$—CO—). The identity with the unsaturated XI derived from XXI was confirmed by TLC, MS and NMR comparison.

Compound XII as colourless needles (from light petroleum), m.p. 101–104°, MS m/e: 222 (M^+), CD (c = 0·0486, methylcyclohexane-isopentane(1:3)): $[\theta]_{293}^{20°}$ −1520, $[\theta]_{290}^{-158°}$ −2150, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1708 (cycloheptanone), NMR (CCl_4): two 3H d at 0·86, 0·89 (J = 7, $(C\underline{H}_3)_2CH$—), 3H s at 0·91 ($C\underline{H}_3$—C<), 3H s at 1·25 ($C\underline{H}_3$—C<), NMR ($CDCl_3$): two 3H d at 0·83, 0·94 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 0·90 ($C\underline{H}_3$—C<), 3H s at 1·27 ($C\underline{H}_3$—C<), NMR (C_6H_6): two 3H d at 0·78, 0·86 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 0·82 ($C\underline{H}_3$—C<), 3H s at 1·00 ($C\underline{H}_3$—C<).

Partial hydrogenation of (+)-α-*cyperone over Adams' catalyst in methanol.* The ketone XV (1·04 g) in MeOH (10 ml) was hydrogenated over PtO_2 (20 mg). After the consumption of H_2 (1 mole) the catalyst was filtered off and the solvent distilled off to give XVI as a colourless oil (1·05 g), d_4^{25} 0·975, n_D^{25} 1·513, $[\alpha]_D$ +130·4°, UV λ_{max}^{EtOH} mμ (log ε): 251 (4·20), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1664, 1613 (cyclohexenone), NMR (CCl_4): 6H d at 0·96 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 1·20 ($C\underline{H}_3$—C<), 3H s at 1·72 ($C\underline{H}_3$—C=C).

The semicarbazone, prepared in the usual manner ($NH_2NHCONH_2 \cdot HCl$—AcONa—H_2O—EtOH), crystallized from EtOH as colourless needles, m.p. 207–209°. (Found: C, 69·15; H, 9·79; N, 15·30. Calc. for $C_{16}H_{27}ON_3$: C, 69·27; H, 9·81; N, 15·15%).

The 2,4-dinitrophenylhydrazone, ($NH_2NHC_6H_3(NO_2)_2$—H_2SO_4—EtOH), crystallized from AcOEt as dark red flat needles, m.p. 170–171°. (Found: C, 62·72; H, 6·98; N, 14·00. $C_{21}H_{28}O_4N_4$ requires: C, 62·98; H, 7·05; N, 13·99%).

Huang-Minlon reduction of dihydro-α-cyperone. The ketone XVI (2·1 g) and 90% $NH_2NH_2 \cdot H_2O$ (1 g) in EtOH (7 ml) were refluxed for 1 hr. After the addition of KOH (5 g) and triethylene glycol (5 ml), $NH_2NH_2 \cdot H_2O$ and EtOH were then removed by distillation and the mixture was kept at 190–200° for 8·5 hr. The product was isolated with ether as usual and distilled under reduced press to give a mixture of eudesm-4-ene and eudesm-3-ene as a colourless oil, d_4^{25} 0·902, n_D^{25} 1·491, $[\alpha]_D$ +57·8°; IR ν_{max}^{liquid} cm^{-1}: 1661 (ethylene), NMR (CCl_4): 6H d at 0·92 (J = 7, $(C\underline{H}_3)_2CH$—), 3H s at 1·00 ($C\underline{H}_3$—C<), 3H s at 1·58 ($C\underline{H}_3$—C=C), ~0·3 H m at 5·29 (—CH_2—C$\underline{H}$=C<).

Thioketalization of dihydro-α-cyperone. The ketone XVI (2·7 g), $HSCH_2CH_2SH$ (1·6 g) and $BF_3 \cdot Et_2O$ (5 ml) were set aside at room temp for 24 hr. The product was worked up in the usual manner to afford XVII as a colourless oil (3·3 g), NMR (CCl_4): 6H d at 0·90 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 1·04 ($C\underline{H}_3$—C<), 3H s at 1·82 ($C\underline{H}_3$—C=C), 4H m at 3·1–3·6 (—S—$(CH_2)_2$—S—).

Reduction of dihydro-α-cyperone ethylene thioketal with Raney nickel. The thioketal XVII (1·5 g) in EtOH (30 ml) was refluxed with Raney Ni (15 g) for 24 hr. After isolation, the product was distilled under diminished press to give XVIII as a colourless oil (0·8 g), $[\alpha]_D$ +71·8° (c = 3·41). NMR (CCl_4):6H d at 0·94 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 0·99 ($C\underline{H}_3$—C<), 3H br s at 1·56 ($C\underline{H}_3$—C=C).

Epoxidation of eudesm-4-ene with perbenzoic acid. The hydrocarbon XVIII (0·8 g) was treated with BzOOH (0·95 g) in $CHCl_3$ (19 ml) at room temp for 5 min and yielded a mixture of XIX and XX which was chromatographed over silica gel (15 g).

Elution with light petroleum afforded XIX as a colourless oil, $[\alpha]_D$ +63·9° (c = 2·82), NMR (CCl_4): 6H d at 0·89 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 1·01 ($C\underline{H}_3$—C<), 3H s at 1·20 ($C\underline{H}_3$—C<O>C<).

Elution with the same solvent yielded XX as a colourless oil, $[\alpha]_D$ +11·9 (c = 6·03). NMR (CCl_4): 6H d at 0·87 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 0·98 ($C\underline{H}_3$—C<), 3H s at 1·23 ($C\underline{H}_3$—C<O>C<).

Rearrangement of 4α,5α-epoxy-eudesmane with boron trifluoride etherate. The epoxide XIX (20 mg) in benzene (0·5 ml) was treated with $BF_3 \cdot Et_2O$ (0·2 ml) at room temp for 4 min. Ether extraction followed by silica gel chromatography afforded XXI as a colourless oil (10 mg), MS m/e: 222 (M^+), $[\alpha]_D$ +41·9° (c = 4·29), ORD (c = 0·127, MeOH): $[\phi]_{504}^{peak}$ +1490, $[\phi]_{263}^{trough}$ −1330, CD (c = 0·1063, methylcyclohexane-isopentane = 1:3): $[\theta]_{294}^{20°}$ +1850, $[\theta]_{290}^{-180°}$ +1900; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1694 (cycloheptanone), NMR (CCl_4): two 3H d at 0·88, 0·91 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 1·07 ($C\underline{H}_3$—C<), 3H s at 1·14 ($C\underline{H}_3$—C<), NMR ($CHCl_3$): 6H d at 0·87 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 1·09 ($C\underline{H}_3$—C<), 3H s at 1·14 ($C\underline{H}_3$—C<), NMR (C_6H_6): two 3H d at 0·76, 0·79 (J = 6, $(C\underline{H}_3)_2CH$—), 3H s at 0·92 ($C\underline{H}_3$—C<), 3H s at 0·93 ($C\underline{H}_3$—C<), NMR (C_5H_5N): two 3H d at 0·80, 0·82 $(CH_3)_2CH$—), 3H s at 1·05 ($C\underline{H}_3$—C<), 3H s at 1·07 ($C\underline{H}_3$—C<).

Rearrangement of 4β,5β-epoxy-eudesmane with boron trifluoride etherate. The epoxide XX (66 mg) in benzene (0·5 ml) was treated with BF_3—Et_2O (0·3 ml) at room temp for 6 min. The isolated product (67 mg) was chromatographed over silica gel. Elution with light petroleum–benzene (5:1) followed by distillation under reduced press gave XI as a colourless oil, MS m/e: 222 (M^+), $[\alpha]_D$ +38·5° (c = 4·05); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1718, 1360 (acetyl), NMR (CCl_4): 6H d at 0·88 (J = 6, $(C\underline{H}_3)_2CH$—), 3H br s at 1·56 ($C\underline{H}_3$—C=C), 3H s at 2·02 ($C\underline{H}_3$—CO—). Tetranitromethane test: positive.

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