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TERPENOIDS—LXIII

RING CONTRACTION IN CADINENIC AND SELINENIC COMPOUNDS*

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Abstract—Several cadinenic and selinenic epoxides on treatment with BF_3–ethereate have been found to undergo ring contraction resulting in the formation of fully substituted aldehydes. Structures of these compounds have been decided on the basis of chemical and spectral evidences.

RECENTLY, several antipodal sesquiterpenoids have been isolated from Indian vetiver oil.[1] A series of ketonic compounds have been prepared from the antipodal cadinenic alcohol khusinol[1a] (I), with the ketogroup in different positions in order to study their optical rotatory dispersion and so elucidate certain stereo chemical features.

Although the conversion of an epoxy compound to the corresponding ketone by treatment with BF_3–ethereate has been employed with considerable success in steroids[2] and terpenoids,[3,4] there are several limiting features for this conversion, the success of which depends on the nature and position of the double bond from which the epoxy compound is prepared. In the case of cadinenic compounds related to khusinol (I), the ultimate product is not the expected ketone, but a fully substituted aldehyde formed through contraction of a six-membered to a five-membered ring. Once this was realized, the isomerization reaction was applied to cadinenic and selinenic terpenoids and in every case this ring contraction was observed. The results are presented in this communication.

The formation of epoxide in individual cases was confirmed by examination of IR spectra of the starting material and the corresponding epoxide formed and unless it crystallized out spontaneously no attempt was made to purify it further so as to avoid any isomerization to the corresponding ketone,[5,6] the presence of which would interfere in the isolation of the aldehyde formed through ring contraction. For this reason, the epoxy compounds were immediately treated with BF_3–ethereate followed by other operations.

Dihydrokhusinol (II), obtained by partial hydrogenation of khusinol (I), on reacting with excess perbenzoic acid gives the epoxide (III), which on subsequent treatment

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[1a] A. A. Rao, K. L. Surve, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron* **19**, 233 (1963);
[b] C. C. Kartha, P. S. Kalsi, A. M. Shaligram, K. K. Chakravarti and S. C. Bhattacharyya, *Ibid.* **19**, 241 (1963);
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[2] H. B. Henbest and T. I. Wrigley, *J. Chem. Soc.* 4596 (1957).

[3] D. H. R. Barton, O. C. Böckman and P. de Mayo, *J. Chem. Soc.* 2263 (1960).

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[6] Tiffeneau and Levy, *Bull. Soc. Chim. Fr.* (4), **49**, 1806 (1931).

with freshly distilled BF_3–ethereate is converted to the crystalline hydroxy aldehyde (V), $C_{15}H_{26}O_2$, m.p. 132–133° and characteristic IR bands at 2703 and 1712 cm^{-1}. In conformity with its structure, it is reduced to the corresponding diol (VI), $C_{15}H_{28}O_2$, m.p. 154–156°, which on oxidation with Jones reagent[7] is converted to the cyclopentanone (VIII), formed, presumably, via decarboxylation of the intermediate β-keto-carboxylic acid (VII).

Dihydrokhusinol (II) on treatment with chromic acid is converted to the corresponding $\alpha\beta$- unsaturated ketone (IX), which on oxidation with alkaline hydrogen peroxide[8] gives the epoxy ketone (X). On treatment with BF_3–ethereate, X rearranges to the keto-aldehyde (XI), $C_{15}H_{24}O_2$, m.p. 74–75°. In addition to a strong band at 1742 cm^{-1} ascribable to a keto group on a five-membered ring, the IR spectrum (Fig. 1) shows bands at 2725 and 1709 cm^{-1} due to an aldehyde function. An inflection at 1422 cm^{-1} is attributable to a —CO—CH_2— grouping. Chromatography of this keto-aldehyde through slightly alkaline alumina results in decarbonylation[9] to the ketone (VIII) with a single peak in VPC and in conformity with its structure a NMR signal at 7·8τ (3H) due to three protons α to the carbonyl group. Its IR spectrum (Fig. 1) shows an intense band at 1730 cm^{-1} due to a keto group in a five membered ring. It easily forms a semicarbazone $C_{15}H_{27}N_3O$, m.p. 194–195°. On reduction with lithium aluminium hydride, XI converts to a crystalline diol (XII), $C_{15}H_{28}O_2$, m.p. 183–184°, possibly epimeric with the diol, VI. The IR spectra of the diols VI and XII are nearly identical, but their rotations and m.p. are different.

(—)-γ-Cadinene[1a] (XIII) when treated with one mole perbenzoic acid, undergoes partial epoxidation at the trisubstituted double bond to yield the monoepoxide (XIV), which retains the methylenic double bond, as shown by IR bands at 1642 and 892 cm^{-1} The epoxide on treatment with BF_3–ethereate gives the aldehyde (XV), $C_{15}H_{24}O$, via ring contraction and simultaneous migration of the methylenic double bond to the tetrasubstituted position. The IR spectrum shows bands at 2710 and 1720 cm^{-1} due to the aldehyde function, but no bands at 1642 and 892 cm^{-1}, which are present prior to BF_3 treatment. The NMR spectrum (Fig. 11) fully substantiates the structure and clearly shows the presence of a methyl group on a tetrasubstituted double bond.

The epoxide of (—) dihydro-γ-cadinene[1a] (XVI) undergoes ring contraction to the aldehyde (XVII), $C_{15}H_{26}O$, in a pure state (VPC). The IR spectrum (Fig. 1) shows bands at 2725 and 1724 cm^{-1}, characteristic of an aldehyde group. On reduction with lithium aluminium hydride it is converted to the alcohol (XVIII), $C_{15}H_{28}O$, which easily forms the acetate (XIX) $C_{17}H_{30}O_2$. The structures of XVII, XVIII and XIX are fully substantiated by their IR and NMR spectra.

The epoxide of tetrahydrokhusilene (XX), prepared from the aldehyde khusilal,[10] undergoes ring contraction to the aldehyde (XXII), $C_{14}H_{24}O$ with characteristic IR bands for an aldehyde function.

α-Santenolide (XXIII), the only selinenic compound examined was obtained* from costunolide[11] and on treatment with perbenzoic acid yields crystalline epoxide (XXIV),

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* The sample was kindly supplied by Mr. G. H. Kulkarni of our laboratory.

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[9] H. O. House and R. L. Wasson, *J. Amer. Chem. Soc.* **78,** 4394 (1956); **79,** 1488 (1957).

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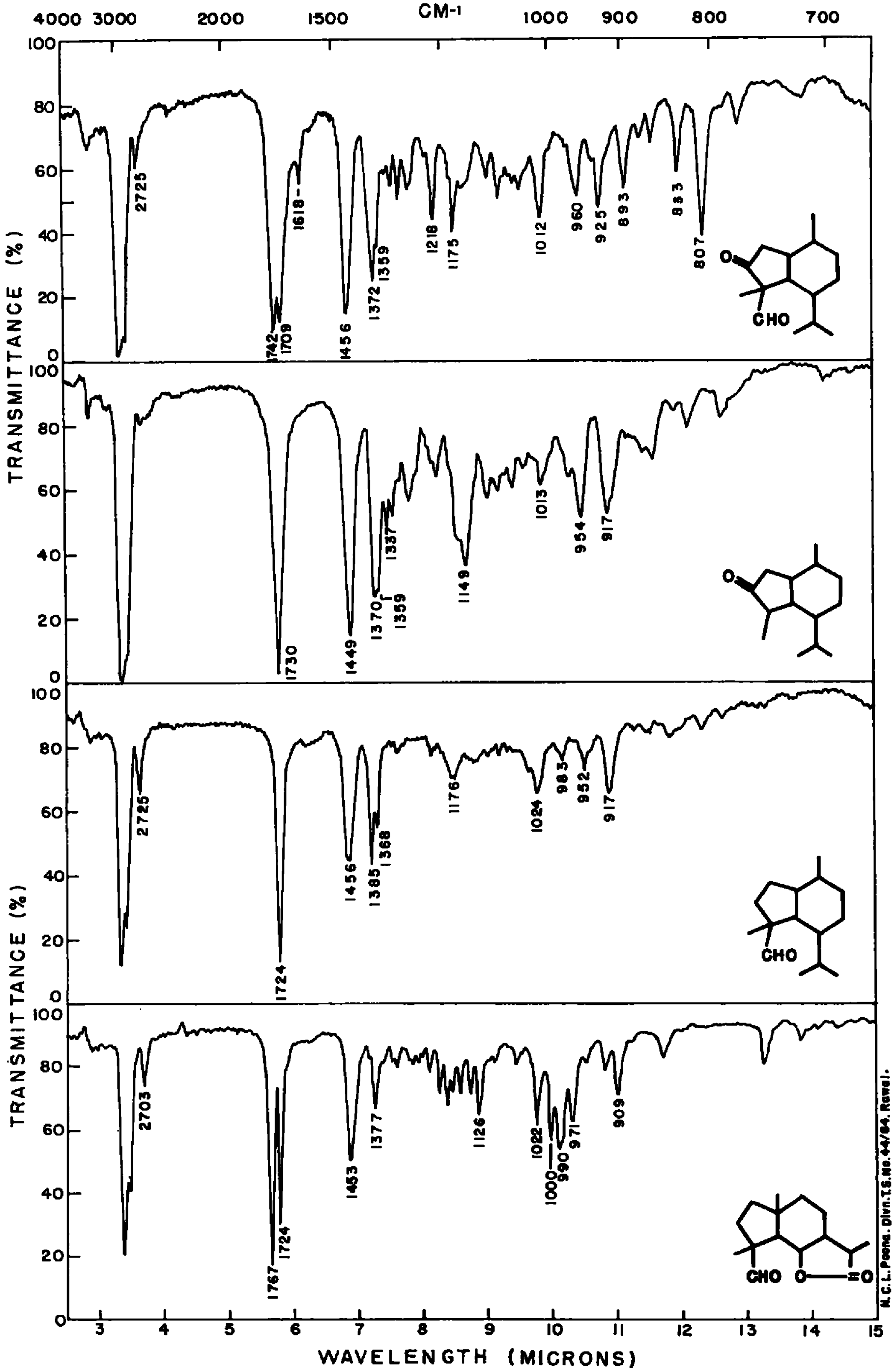
CM-1
4000
3000
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TRANSMITTANCE (%)
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2725
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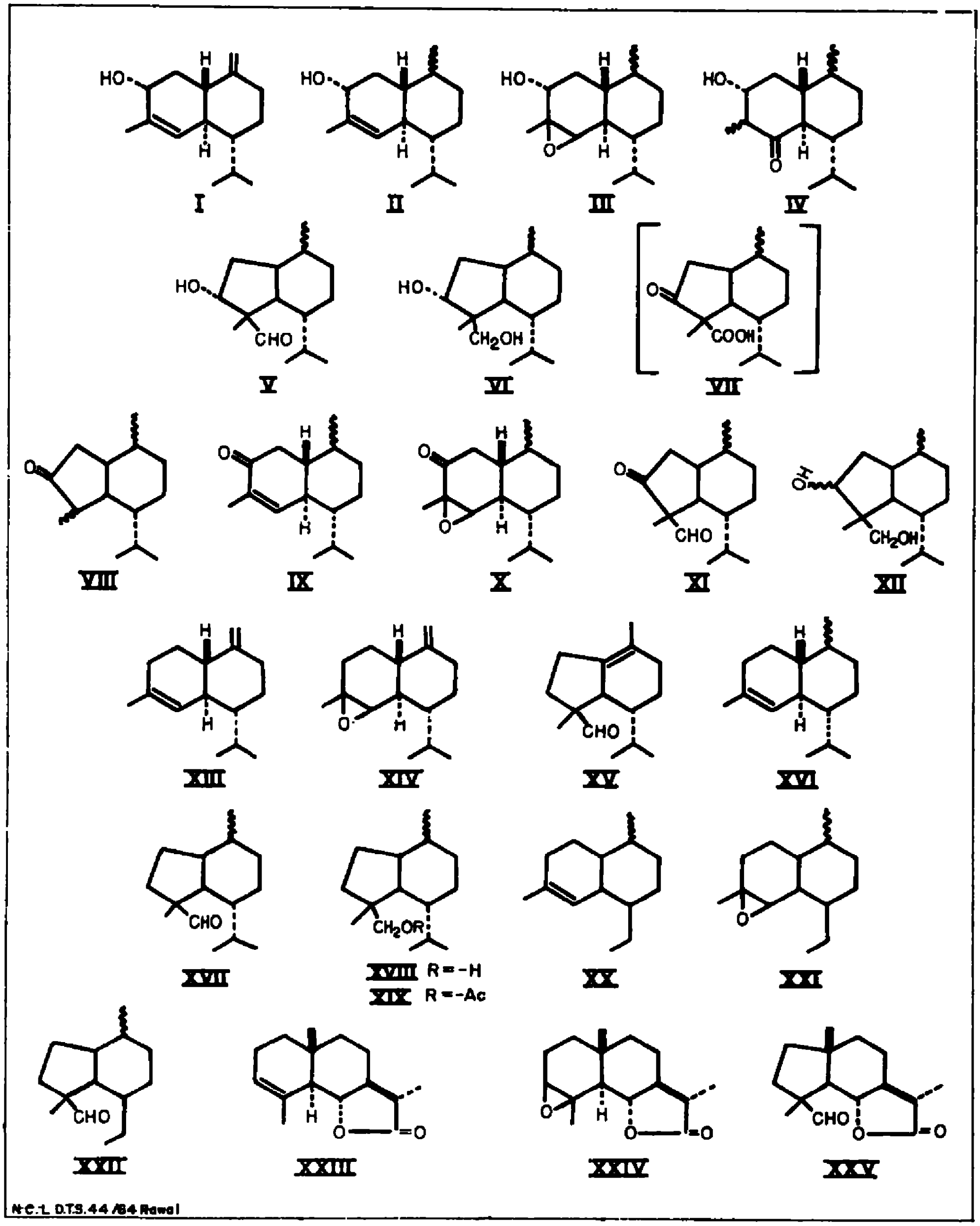
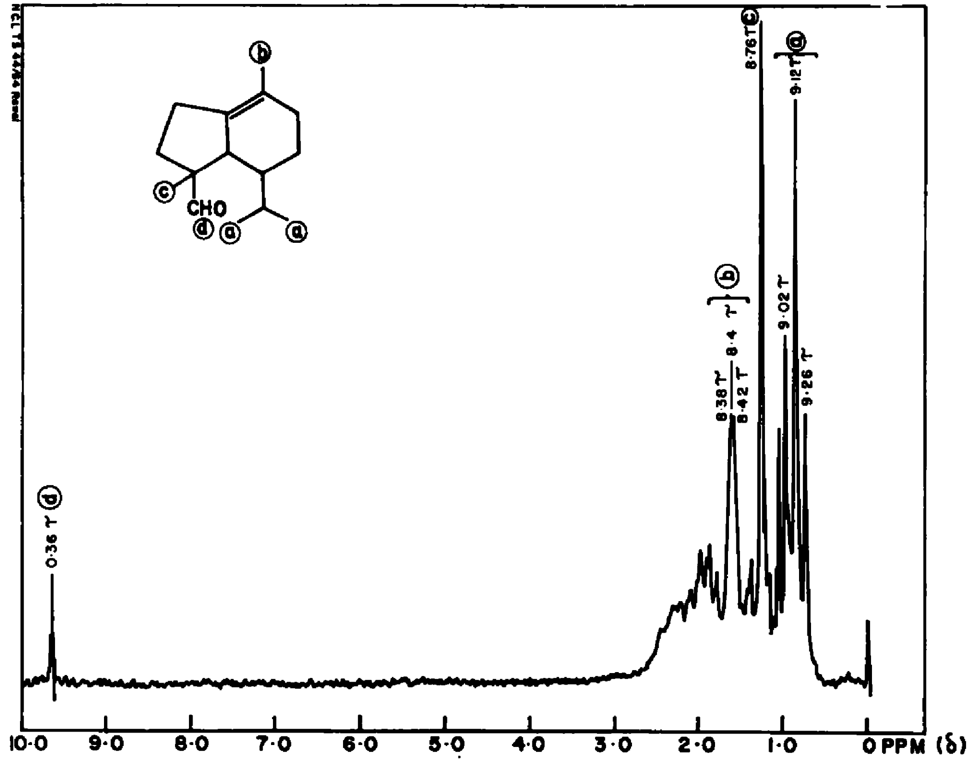
m.p. 75–77°. The action of BF_3-ethereate results in the formation of the aldehyde (XXV), $C_{15}H_{22}O_3$, m.p. 135–136°, the IR spectrum (Fig. 1) of which shows bands at 2703 and 1724 cm^{-1} for the aldehyde group and also an intense band at 1767 cm^{-1} due to the γ-lactone function. The NMR spectrum (Fig. III) is in conformity with its structure and XXV readily forms a semicarbazone, $C_{16}H_{25}N_3O_3$, m.p. 231–232°.




ⓑ
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0·36 τ ⓓ
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9·02 τ
9·12 τ ⓐ
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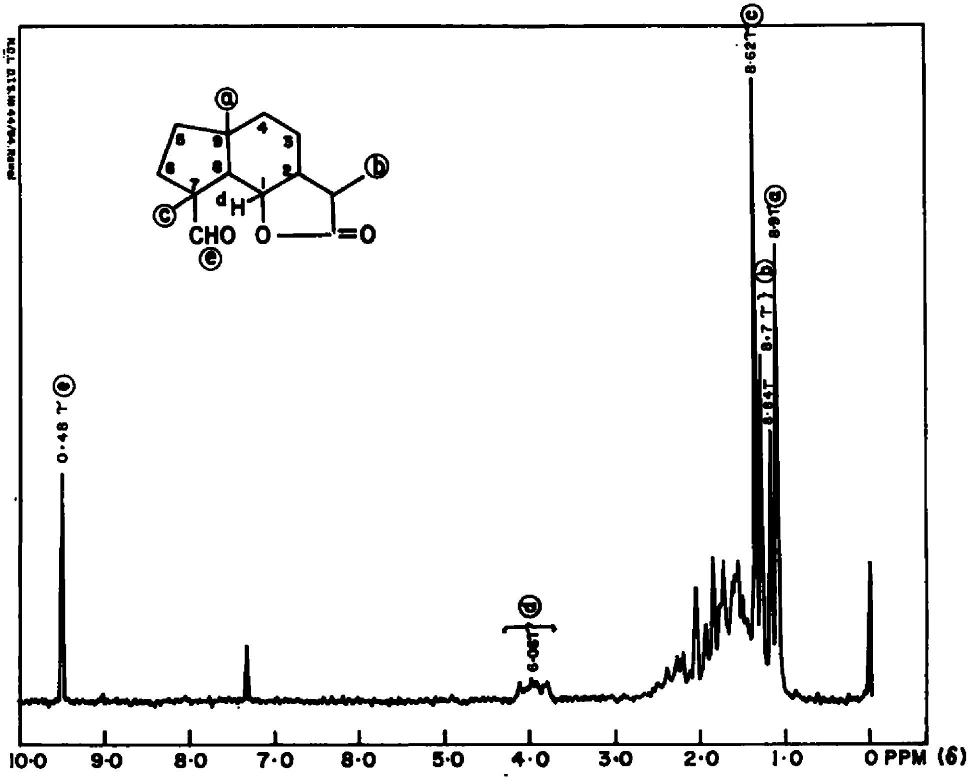
FIG. 2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ⓒ
d H
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O
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0·48 τ ⓔ
6·06 τ ⓓ
8·62 τ ⓒ
8·7 τ ⓑ
8·84 τ
8·91 ⓐ
10·0
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3·0
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0 PPM (6)

FIG. 3

Ring contractions of a similar nature have been reported[9,12] for epoxides of αβ-unsaturated ketones and the mechanism has also been recorded.[9] Recently, ring contraction has been observed in simple monoterpenes[13] and also in a new triterpenoid, serratenediol.[14] Also the Grignard reaction on certain steroidal epoxides[15] leads through ring contractions to the formation of nor-steroids.

The stereochemistry of the various products formed during the present investigation is receiving attention.

EXPERIMENTAL

The m.p. and b.p. are uncorrected. Rotations were measured in $CHCl_3$. The IR spectra were taken in thin films or in the case of solids as nujol mulls unless otherwise stated on a Perkin-Elmer infracord spectrophotometer, model 137B, with NaCl optics. NMR spectra were recorded on a 60 m.c. Varian instrument in CCl_4 solution or in $CDCl_3$ solution as the case may be with T.M.S. as internal standard. GLC analyses were carried out on a Griffin VPC apparatus MK IIA, with polyester column employing H_2 as the carrier gas.

Epoxy alcohol (III) *from dihydrokhusinol* (II). Dihydrokhusinol (4·5 g) in $CHCl_3$ (15 ml) was treated with a chloroform solution of perbenzoic acid (80 ml; 0·6 N) and kept at 0° for 24 hr. The solution was washed with $NaHCO_3$ aq, water and dried. Evaporation of solvent gave the epoxy alcohol (III, 4·3 g). IR bands at: 3448, 1460, 1374, 1361, 1266, 1212, 1172, 1117, 1095, 1042, 1010, 909, 877, 840, 826, 807, 752, 714 cm^{-1}.

Hydroxy aldehyde (V) *from epoxy alcohol* (III). To a solution of the epoxy alcohol (4·3 g) in dry benzene (50 ml) freshly distilled BF_3–ethereate (3 ml) was added and the mixture kept at room temp for 1 hr. The reaction mixture was then diluted with water (100 ml) and extracted with ether. The ethereal layer was washed with water, dried (Na_2SO_4) and after evaporation of the solvent, the crude hydroxy aldehyde (4·0 g) was passed through a column of alumina (grade III, 120 g) and the ether fraction on concentration gave the crystalline hydroxy aldehyde (2·8 g). This was crystallized from pet. ether* and finally purified by sublimation *in vacuo*, m.p. 132–133°, $(\alpha)_D$ −30·3° (*c*, 4·28). (Found: C, 75·77; H, 11·09. $C_{15}H_{26}O_2$ requires: C, 75·58; H, 11·0%). In its NMR spectrum, the hydroxy aldehyde showed signals at 0·54τ (1H, —C*H*O), 6·17τ (1 H, C*H*OH), 7·62τ (1H, CHO*H*) 8·76τ $\left(3H, >C\text{—}CH_3\right)$, 9·06, 9·08, 9·16, 9·2 and 9·28τ $\left(3H, >CHCH_3 \text{ and } 6H, \text{—}CH\begin{matrix} CH_3 \\ CH_3 \end{matrix}\right)$. IR (in nujol) bands at: 3226, 2703, 1712, 1451, 1374, 1361, 1112 cm^{-1}.

Diol (VI) *from hydroxy aldehyde* (V). Hydroxy aldehyde (0·5 g) in dry ether (50 ml) was refluxed for 8 hr with $LiAlH_4$ (0·17 g). Excess $LiAlH_4$ was decomposed by careful addition of moist ether and the product taken up in ether, washed successively with dil. HCl aq, $NaHCO_3$ aq and finally with water and dried. After removal of the solvent, the residue (0·49 g) was crystallized from alcohol and sublimed *in vacuo*, m.p. 154–156°; $(\alpha)_D$ −25·8 (in ethanol; *c*, 1·94). (Found: C, 74·8; H, 11·98. $C_{15}H_{28}O_2$ requires: C, 74·95; H, 11·74%). IR (in nujol) bands at: 3401, 1253, 1215, 1170, 1124, 1111, 1038, 1000, 970, 926 cm^{-1}.

Epoxy ketone (X) *from ketone* (IX). The ketone (5 g) in methanol (60 ml) and H_2O_2 (15 ml; 30%) was treated with NaOH aq (6 ml; 6N) during 1 hr and the mixture stirred well for 3 hr at 20–25°. The product was extracted with ether, the ethereal extract washed free of alkali, and the epoxy ketone obtained after ether removal. IR bands at: 1698, 1460, 1383, 1362, 1282, 1235, 1176, 1124, 1075, 1036, 1024, 1000, 926, 909, 877, 848, 813, 787, 709 cm^{-1}.

Keto-aldehyde (XI) from epoxy ketone (X). The epoxy ketone (4·5 g) in dry benzene (50 ml) was treated with freshly distilled BF_3–ethereate (2 ml) and the mixture after standing at room temp for 30 min was processed to give the keto aldehyde (2·84 g), as a crystalline solid. It was purified by

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* Unless otherwise stated pet. ether refers to the fraction b.p. 60–80°.

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[15] P. Narasimha Rao and James C. Uroda, *Tetrahedron Letters* **19**, 1117 (1964).

crystallizations from pet. ether followed by sublimation *in vacuo*, m.p. 74–75°; $(\alpha)_D$ −43° (*c*, 2·24). (Found: C, 75·98; H, 10·17. $C_{15}H_{24}O_2$ requires: C, 76·22; H, 10·24%). IR (Fig. 1; in nujol) bands at: 2725, 1742, 1709, 1456, 1372, 1359, 1218, 1175, 1012, 960, 925, 893, 833, 807 cm^{-1}.

Ketone (VIII) *from keto aldehyde* (XI). The keto aldehyde (0·5 g) was chromatographed over slightly alkaline alumina (grade II, 15 g) and the column eluted with pet. ether. This fraction on concentration gave the ketone (0·35 g), as a liquid product, which was purified by distillation *in vacuo*, b.p. 105° (bath)/0·7 mm, n_D^{30} 1·4750, $(\alpha)_D$ −9·6° (*c*, 3·47). (Found: C, 80·3; H, 11·41. $C_{14}H_{24}O$ requires: C, 80·71; H, 11·61%). VPC analysis showed a single peak. The NMR spectrum showed the presence of three protons α to the carbonyl and they appear between 7·7 and 7·9τ. IR (Fig. 1) bands at: 1730, 1449, 1370, 1359, 1228, 1212, 1149, 1337, 1013, 954, 917 cm^{-1}. An inflection at 1422 cm^{-1} is attributable to a —CO—CH$_2$— grouping. This ketone easily formed a semicarbazone $C_{15}H_{27}N_3O$, m.p. 194–95° (Found: N, 16·01; $C_{15}H_{27}N_3O$ requires: N, 15·9%).

Diol (XII) *from keto aldehyde* (XI). The keto aldehyde (0·4 g) in dry ether (40 ml) was refluxed for 10 hr with $LiAlH_4$ (0·15 g) and excess decomposed by careful addition of moist ether and the product extracted with ether and worked up in the usual way yielding the diol (0·38 g) which crystallized from alcohol and sublimed *in vacuo*, m.p. 183–184°; $(\alpha)_D$ + 41·3° (ethanol C, 0·775). (Found: C, 75·21; H, 11·87. $C_{15}H_{28}O_2$ requires: C, 74·95; H, 11·74%). IR (in nujol) bands at: 3413 (intense band), 1449, 1372, 1359, 1212, 1163, 1112, 1043, 999, 974, 936 cm^{-1}.

Ketone (VIII) *from diol* (VI). To a solution of the diol (0·15 g) in dry acetone (15 ml), Jones' reagent (0·2 ml) was added dropwise until a pale yellow colour persisted. The mixture was left at room temp for 15 min and a few drops methanol added and the mixture diluted with water. Repeated extraction with ether followed by removal of solvent gave the ketone (0·095 g) which was identified as VIII obtained from keto-aldehyde (XI) by VPC analysis under identical conditions.

Monoepoxide (XIV) *of* (−)*-γ-cadinene* (XIII) *and its conversion to aldehyde* (XV). (−)-γ-Cadinene (3·7 g) in $CHCl_3$ (25 ml) on treatment with one mole perbenzoic acid (50 ml; 0·735 N) at 0° for 12 hr furnished the monoepoxide (3·5 g). The monoepoxide (3·5 g) dissolved in dry benzene (40 ml) was treated with freshly distilled BF_3–ethereate (2 ml) and kept at room temp for 15 min. The crude product was chromatographed over alumina (grade II, 130 g) and the pet. ether fraction on concentration gave the aldehyde (1·7 g) which was distilled *in vacuo*, b.p. 125° (bath)/2 mm, n_D^{30} 1·4940; $(\alpha)_D$ - 18·9° (*c*, 2·402). (Found: C, 81·45; H, 10·55. $C_{15}H_{24}O$ requires: C, 81·7; H, 10·98%). In the NMR spectrum (Fig. II) the aldehyde proton appears at 0·36τ. A triplet centred around 8·4τ (J = 2 c/s) corresponding to three protons is attributable to the methyl group on the double bond and results from coupling with the allylic methylene protons. The quarternary methyl group on the carbon carrying the aldehyde group appears at 8·76τ (3 H). The isopropyl group appears as a triplet at 9·02, 9·12 and 9·26τ (6H). IR bands at: 2710, 1720, 1449, 1370, 1361, 1321, 1205, 1170, 1110, 1013, 909 cm^{-1}.

(−) *Dihydro-γ-cadinene* (XVI) *from dihydro khusinol* (II). Dihydrokhusinol (obtained from khusinol) by partial hydrogenation showed two spots (TLC). On repeated crystallizations from pet. ether dihydrokhusinol was obtained in a pure state (TLC). Dihydrokhusinol (5 g) on tosylation and detosylation in the usual way gave (−) dihydro-γ-cadinene (2·95 g). The hydrocarbon was distilled over Na, b.p. 138° (bath)/6 mm, n_D^{30} 1·4954; $(\alpha)_D$ +44·3°. (Found: C, 87·22; H, 12·31. $C_{15}H_{26}$ requires: C, 87·32; H, 12·69%), VPC analysis showed a single peak.

Conversion of the epoxide of (−) *dihydro-γ-cadinene* (XVI) *to aldehyde* (XVII). The epoxide (2·7 g) of (−) dihydro-γ-cadinene (2·75 g), prepared by perbenzoic acid treatment, was dissolved in dry benzene (25 ml) and freshly distilled BF_3–ethereate (1·5 ml) added. The mixture after standing at room temp for 15 min furnished the crude aldehyde (2·6 g) which was purified by passing through a column of alumina (grade II, 70 g) and eluting with pet. ether. It was finally distilled *in vacuo* (1·18 g), b.p. 120° (bath)/2 mm, n_D^{25} 1·4822; $(\alpha)_D$ +28·4° (*c*, 3·49). (Found: C, 81·21; H, 11·80. $C_{15}H_{26}O$ requires: C, 81·02; H, 11·71%). In the NMR spectrum it showed signals at 0·24τ (1H, —C*H*O) $8{\cdot}78\tau\left(3H, \gt CCH_3\right)$ 9·06, 9·14, 9·20, 9·24 and $9{\cdot}28\tau\left(3H, \gt CHCH_3,\ 6H, \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!\gt CH—\right)$.

Alcohol (XVIII) *from aldehyde* (XVII). The aldehyde (0·43 g) in dry ether (50 ml) was refluxed with $LiAlH_4$ (0·2 g) for 10 hr. The product (0·425 g) on passing through alumina (grade III, 20 g) and eluting with ether gave the alcohol (0·402 g), b.p. 125° (bath)/ 0·8 mm, n_D^{28} 1·4918; $(\alpha)_D$ +20·4° (*c*, 3·12), (Found: C, 79·93; H, 12·99. $C_{15}H_{28}O$ requires: C, 80·29; H, 12·58%). In its NMR spectrum the alcohol showed signals at 6·57τ (2H, $-\mathit{CH}_2\mathrm{OH}$), 7·74τ (1H, $-\mathrm{CH_2O}\mathit{H}$), 8·97τ $\left(\mathrm{3H}, -\!\!>\!\mathrm{C}\mathit{CH}_3\right)$, 9·04, 9·12, 9·13, 9·23 and 9·25τ $\left(\mathrm{3H}, >\!\mathrm{CH\text{-}C}\mathit{H}_3, \mathrm{6H}, -\mathrm{CH}\Big\langle\begin{matrix}\mathit{CH}_3\\ \mathit{CH}_3\end{matrix}\right)$. IR bands at: 3413, 1460, 1379, 1364, 1031, 1020 cm^{-1}.

Acetate (XIX) *from alcohol* (XVIII). The alcohol (0·29 g) in dry pyridine (20 ml) and acetic anhydride (4 ml) was kept at room temp for 24 hr and then poured onto crushed ice. The crude product (0·28 g) was chromatographed over alumina (grade II, 15 g) and eluted with pet. ether. The acetate was finally distilled *in vacuo*, b.p. 150° (bath)/2 mm, n_D^{28} 1·4758; $(\alpha)_D$ +20·5°. (Found: C, 77·36; H, 11·11. $C_{17}H_{30}O_2$ requires: C, 76·64; H, 11·35%). The NMR spectrum showed signals at 6·1τ (2H, $\mathrm{C}\mathit{H}_2\mathrm{O.CO.CH_3}$), 8·02τ (3H, $\mathrm{CH_2O.\ CO.C}\mathit{H}_3$), 8·86τ $\left(\mathrm{3H}, -\!\!>\!\mathrm{C\text{-}C}\mathit{H}_3\right)$, 9·02, 9·11, 9·13, 9·24, and 9·26τ $\left(\mathrm{3H}, >\!\mathrm{CH{-}CH_3}; \mathrm{6H}, \begin{matrix}\mathit{CH}_3\\ \mathit{CH}_3\end{matrix}\Big\rangle\mathrm{CH}-\right)$. IR bands at: 1754, 1471, 1391, 1374, 1238, 1038, 984 cm^{-1}.

Epoxide (XXI) *of tetrahydrokhusilene* (XX) *and its conversion to aldehyde* (XXII). Khusilene obtained from khusilal,[10] on partial hydrogenation gave the tetrahydrokhusilene. Tetrahydrokhusilene (0·8 g) dissolved in $CHCl_3$ (10 ml) on treatment with excess of perbenzoic acid (30 ml; 0·35 N) at 0° for 12 hr gave the epoxide (0·79 g). The epoxide (0·79 g) in dry benzene (15 ml) was treated with BF_3–ethereate (0·7 ml) to give the crude aldehyde (0·785 g) which was purified by chromatography over alumina (grade II, 20 g). The aldehyde (0·35 g) was distilled *in vacuo*, b.p. 115–120° (bath)/0·7 mm, n_D^{30} 1·4879; $(\alpha)_D$ +20·9°. (Found: C, 79·89; H, 11·61. $C_{14}H_{24}O$ requires: C, 80·71; H, 11·61%). IR bands at: 2703, 1724, 1449. 1370 cm^{-1}.

Epoxy α-santenolide (XXIV) *from α-santenolide* (XXIII). α-Santenolide (prepared from costunolide; 1·0 g) was dissolved in $CHCl_3$ (15 ml) and one mole perbenzoic acid (8 ml; 1·19 N) added. The mixture was kept at 0° for 24 hr and yielded the epoxide (0·99 g) as a crystalline product which was purified by crystallization from pet. ether–benzene (2:1) mixture and finally by sublimations in high vacuum, m.p. 75–77°, $(\alpha)_D$ +69·76°. (Found: C, 71·25; H, 8·89. $C_{15}H_{22}O_3$ requires: C, 71·97; H, 8·86%). IR (in nujol) bands at: 1764, 1449, 1370, 1309, 1279, 1250, 1235, 1205, 1144, 1124, 1075, 1053, 1020, 1000, 990, 980, 962, 943, 892, 877, 781, 758, 712 cm^{-1}.

Aldehyde (XXV) *from epoxy α-santenolide* (XXIV). The epoxide (0·8 g) on treatment with BF_3—ethereate gave the aldehyde (0·75 g) which was purified by crystallizations from pet. ether–benzene (2:1) mixture followed by sublimation, m.p. 135–36°, $(\alpha)_D$ +55·33° (*c*, 2·819). (Found: C, 72·31; H, 8·99. $C_{15}H_{22}O_3$ requires: C, 71·97; H, 8·86%). This aldehyde readily formed a semicarbazone, m.p. 231–232°. (Found: N, 13·87. $C_{16}H_{25}N_3O$ requires: N, 13·67%). In the NMR spectrum ($CDCl_3$; Fig. III) the aldehyde proton appears at 0·48τ. A quartet centred around 6·06τ results from the coupling of the C_1 axial proton with C_2 and C_6 axial protons. The signal at 8·62 (3H) is attributable to the methyl group on the carbon atom carrying the aldehyde group. The tertiary methyl group appears as a doublet at 8·7 and 8·84τ (J = 7 c/s) and the angular methyl group shows out at 8·9τ. IR spectrum (in nujol; Fig. 1) bands at: 2703, 1767, 1724, 1453, 1377, 1022, 909 cm^{-1}.