Tetrahedron 1966, Vol. 22, pp. 1641 to 1649. Pergamon Press Ltd. Printed in Northern Ireland

TERPENOIDS—LXXVI

TRANSFORMATION PRODUCTS FROM BF_3-CATALYSED REACTION OF KHUSINOL*

G. K. TRIVEDI, A. D. WAGH, S. K. PAKNIKAR,
K. K. CHAKRAVARTI and S. C. BHATTACHARYYA
National Chemical Laboratory, Poona, India

(*Received* 2 *September* 1965)

Abstract—On the basis of chemical and spectral evidence, the structure II and the absolute configuration XII are assigned to khusinodiol, the principal component obtained by BF_3-ethereate treatment of khusinol (III). The hydrocarbon obtained as a minor product during this reaction has the structure I. Diene monol (XIII), (+)-α-cadinol (XIV) and iso-khusinol (XI) have also been prepared starting from khusinodiol.

BF_3-CATALYZED isomerization, transformation and condensation reactions[1] are well known. This reagent has been employed successfully for the conversion of epoxy compounds to the corresponding ketones in steroids[2,3] and terpenoids.[4,5] Recently this reagent has also been used for ring contraction in cadinenic and selinenic compounds in our laboratory[6] and eleswhere. In this paper we are reporting some of the compounds obtained by treatment of khusinol (III)[7] with BF_3-ethereate.

Khusinol on treatment with BF_3-ethereate in benzene solution at room temperature followed by decomposition with water gives a product which essentially consists of a diol, along with small quantities of keto-alcohols, alcohols, unreacted khusinol and a hydrocarbon fraction.

Chromatography of the hydrocarbon fraction yields in small amount a pure component, $C_{15}H_{22}$, $(\alpha)_D$ $+82{\cdot}58^\circ$, n_D^{29} 1·5180. Its purity was ascertained by TLC and VPC analysis. On dehydrogenation with selenium, this hydrocarbon affords copious amount of cadalene, characterized by its TNB adduct. The IR spectrum (Fig. 1) of this hydrocarbon is identical with that of the hydrocarbon previously obtained by N-lithioethylenediamine reaction of khusinol.[8] Its UV absorption, λ_{max}, 268 mμ (ε 673·3) and λ_{max} 275 mμ (ε 535·1) is in good agreement with the data earlier recorded by Bhattacharyya *et al.*[8] The NMR spectra of the earlier reported product and the

---

* Communication No. 804 from the National Chemical Laboratory, Poona-8, India.

[1] A. V. Topchiev, S. V. Zavgorodnii and Ya M. Paushkin, *International Series of Monographs on organic chemistry* Vol. 2. Pergamon Press (1959).

[2] H. B. Henbest and T. I. Wrigley, *J. Chem. Soc.* 4596 (1957).

[3] J. W. Blunt, M. P. Hartshorn and D. N. Kirk, *Tetrahedron* **21**, 559 (1965).

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

[5] H. Henderson and R. Hodges, *Tetrahedron* **11**, 228 (1960).

[6] C. C. Kartha and K. K. Chakravarti, *Tetrahedron* **21**, 139 (1965).

[7] A. A. Rao, K. L. Surve, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron* **19**, 233 (1963).

[8] B. N. Joshi, R. Seshadri, K. K. Chakravarti and S. C. Bhattacharyya, *Tetrahedron* **20**, 2911 (1964).

present hydrocarbon are also identical except in the isopropyl methyl region. The complex pattern of the NMR spectrum of the former exhibited for the two isopropyl methyls indicates that it presumably is an epimeric mixture at the C_4 carbon atom and this fact gets further confirmation from its low optical rotation.[8a] The NMR spectrum of the hydrocarbon now obtained showed clear signals at 0·69, 0·80, 0·94, 1·05 δ (6H) for the isopropyl methyls; a doublet at 1·2 and 1·32 δ (3H) due to a methyl on a saturated carbon atom; a signal at 2·28 δ (3H) due to a methyl on aromatic ring and a quadruplet at 6·77, 6·91, 7·0, 7·1 δ (3H) attributable to three aromatic protons. These evidences confirm the structure (I) for the hydrocarbon. It appears to be antipodal to calamenene isolated by P. de Mayo *et al.*[8a] from the oil of *Cedrela toona.*

The crystalline diol obtained on chromatography of the reaction product was purified by crystallization followed by sublimation. The diol, $C_{15}H_{26}O_2$, m.p. 133°, $(\alpha)_D$ +23·81°, shows a single spot on TLC. On the basis of IR and NMR spectra, structure (II) is assigned to the diol and which is named as khusinodiol. The IR spectrum (Fig. 1) exhibits absorption bands at 3300, 1120 (hydroxyl group) and 1360, 1380 cm^{-1} (isopropyl side chain). Its NMR spectrum shows signals at 0·70, 0·83, 0·89, 1·0 δ (6H) for the two methyls of the isopropyl group; a signal at 1·28 δ (3H) is due to a methyl on carbon atom bearing oxygen; a signal at 1·67 δ (3H) is for the methyl on a double bond; a broad triplet at 3·7, 3·85 and 3·95 δ (1H) is due to a proton on carbon atom bearing secondary hydroxyl group; signal at 4·95 and 5·19 δ (2H) can be due to two hydroxyl protons and a signal at 5·34 δ (1H) is due to a proton on unsaturated carbon atom (α-hydrogen). When the spectrum was taken in D_2O, the doublet at 4·95 and 5·19 δ due to two hydroxyl protons disappeared and a signal at 4·67 δ due to water appeared.

Khusinodiol (II) furnished a crystalline diol monoacetate, $C_{17}H_{28}O_3$ (IV), m.p. 55°, $(\alpha)_D$ −42°. On oxidation with Jones' reagent,[9] khusinodiol (II) afforded the keto alcohol, $C_{15}H_{24}O_2$ (V), m.p. 90°, $(\alpha)_D$ +163·2°. The UV spectrum shows absorption maximum at 236 mμ (ε 14640) indicating the presence of α,β-unsaturated ketone group Its IR spectrum (Fig. 1) shows bands at 3500, 1129 (tert. hydroxyl group), 1650 (α,β-unsaturated ketone) and 1420 cm^{-1} (—CO—CH_2-group). Khusinodiol on treatment with *p*-toluenesulphonyl chloride in pyridine at room temperature gave the corresponding monotosyl derivative (VI) which on LAH reduction gave a mixture of the alcohols (VII and VIII) indicated by TLC analysis. The diene monol, $C_{15}H_{24}O$, (VII), m.p. 109°, $(\alpha)_D$ +187°, which was formed as the major component[10] was separated from VIII by chromatography over silica gel impregnated with silver nitrate.[11] The UV spectrum showed single absorption at 260 mμ (ε 2606). The IR spectrum is given in Fig. 1. Its NMR spectrum shows signals at 0·68, 0·83, 0·91, 1·0 δ (6H) due to two methyls of the isopropyl group; a signal at 1·13 δ (3H) is observed due to a methyl on a carbon atom carrying oxygen function; a signal at 1·54 δ (1H) appears to be due to hydroxyl proton which disappears when exchanged with D_2O. A methyl group on a

---

[8a] The hydrocarbon[8] reported by Bhattacharyya *et al.* was almost optically inactive and had $(\alpha)_D$ +0·88° while the (−) form of the same hydrocarbon obtained by P. de Mayo, R. E. Williams, G. Büchi and F. H. Feairheller [*Tetrahedron* **21**, 619 (1965)] had $(\alpha)_D$ −68°.

[9] K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C L. Weedon, *J. Chem. Soc.* 39 (1946).

[10] F. G. Jimenez, M. C. Perezamador, S. E. Flores and J. Herran, *Tetrahedron Letters* No. 11, 621 (1965).

[11] A. S. Gupta and Sukh Dev, *J. Chromatography* **12**, 189 (1963).

double bond is exhibited by a signal at 1·74 δ (3H) and signals at 5·48, 5·68, 5·85, 5·98, 6·11 δ (3H) are due to three vinyl protons. Diene monol (VII) on partial hydrogenation over Pd-C in ethanol afforded the monol (+)-α-cadinol (VIII).[12] The purified product analysed for $C_{15}H_{26}O$ and had m.p. 71–74°, $(\alpha)_D$ +64°. Its NMR spectrum showed signals at 0·69, 0·83, 0·87, 0·98 δ (6H) due to two methyls of the isporopyl group; a strong signal at 1·05 δ (3H) due to a methyl on a carbon carrying tertiary hydroxyl group; a methyl on a double bond is indicated by a signal at 1·67 δ (3H) and a signal at 5·48 δ (1H) is due to a hydrogen on unsaturated carbon atom.

As mentioned earlier, khusinodiol (II) furnished a crystalline diol monacetate (IV) which on dehydration with phosphorous oxychloride in pyridine[13] gave a mixture of acetates (two spots on TLC analysis). The first acetate which constitutes more than 80% of the reaction product was separated in the pure form from the other by chromatography (silica gel-$AgNO_3$) and was identified as khusinol-acetate (IX)[7] from its physical properties and its IR spectrum (Fig. 1) which was identical with that of khusinol acetate. On alkaline hydrolysis (IX) gave khusinol (III) identical in all respects with authentic khusinol. The second acetate which constitutes less than 20% of the mixture, on purification (TLC-single spot) analysed for $C_{17}H_{26}O_2$ and had $(\alpha)_D$ −33·64°; n_D^{30} 1·4990. Its IR spectrum (Fig. 1) showed bands at 1742, 1250 cm^{-1} (acetate group) and strong band at 816 cm^{-1} attributed to trisubstituted double bond, but did not exhibit any band due to exocyclic double bond at 1640 and 890 cm^{-1}. The NMR spectrum of the acetate exhibited signals at 0·73, 0·85, 0·88, 1·0 δ (6H) ascribable to the two methyls of the isopropyl group; a strong signal at 1·72 δ (6H) indicates two methyls on double bond; acetate methyl is indicated by a signal at 2·01 δ (3H); a broad triplet at 4·79, 4·92, 5·08 δ (1H) is due to a hydrogen attached to carbon carrying acetate grouping; and a doublet at 5·44, 5·50 δ (2H) is due to two vinyl protons. On the basis of the spectral evidences, structure X was assigned to the new acetate which evidently is a double bond isomer of khusinol acetate (IX). On hydrolysis, X afforded a crystalline alcohol, iso-khusinol, $C_{15}H_{24}O$ (XI), m.p. 87–88°, $(\alpha)_D$ +22·2°. Its IR spectrum (Fig. 1) showed strong band at 820 cm^{-1} (two trisubstituted double bond) and a band at 3500 cm^{-1} (hydroxyl group).

The stereochemistry of the khusinodiol (II) was decided by dehydration experiments described above. The formation of khusinol acetate (IX) as one of the dehydration products in more than 80% yield, suggests that khusinodiol (II) retains the same stereochemistry at all asymmetric centres as that of khusinol (III), except for the carbon atom at C_{10}. The dehydration of the tertiary alcohol yielding khusinol acetate (IX), indicates that the tetriary hydroxyl group is equatorially oriented.[14] Also in the IR spectrum of the khusinodiol C—O stretching frequency occurs at 935 cm^{-1} which is in agreement with the value for 3α-methyl cholesten-3β-ol (940 cm^{-1}).[15] Therefore, khusinodiol (II), diene monol (VII) and monol (VIII) can be represented by the stereoformula XII, XIII and XIV respectively.

---

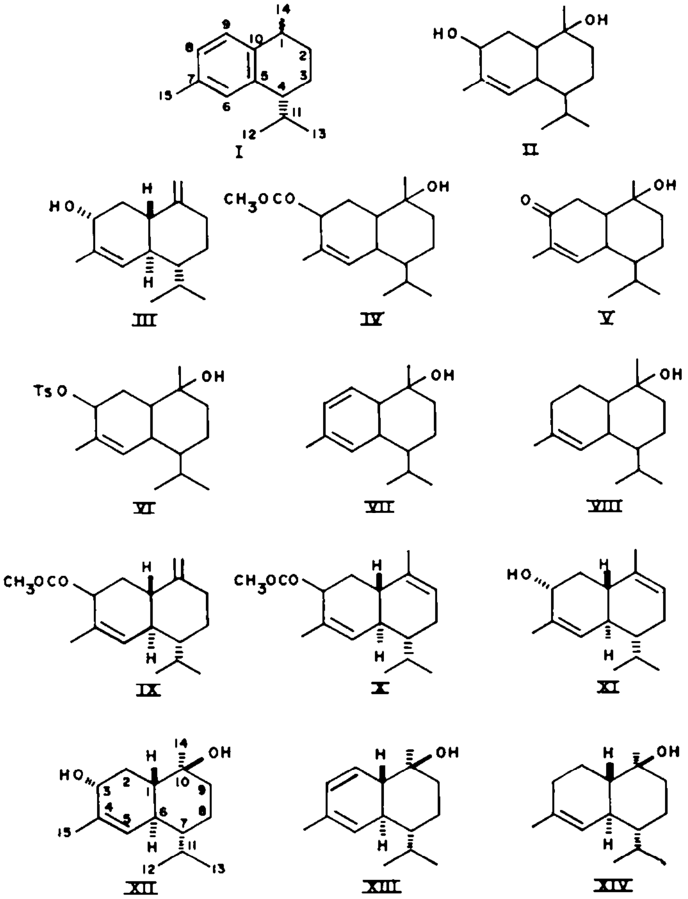
[12] (−) α-Cadinol isolated by Sorm *et al.* have comparable properties excepting its rotation, m.p. 70–74°; $(\alpha)_D$ −47°, refer O. Motl, V. Sykora, V. Herout and F. Sorm, *Coll. Czech. Chem. Comm.* **23**, 1297 (1958).

[13] G. Stork and A. W. Burgstahler, *J. Amer. Chem. Soc.* **77**, 5068 (1955).

[14] G. Buchi, M. Schactl, V. Wittenau and D. M. Wite, *J. Amer. Chem. Soc.* **81**, 1968 (1959).

[15] D. H. R. Barton, A. da S. Campes-Neves and R. C. Cookson, *J. Chem. Soc.* 3500 (1956).

CHART - I



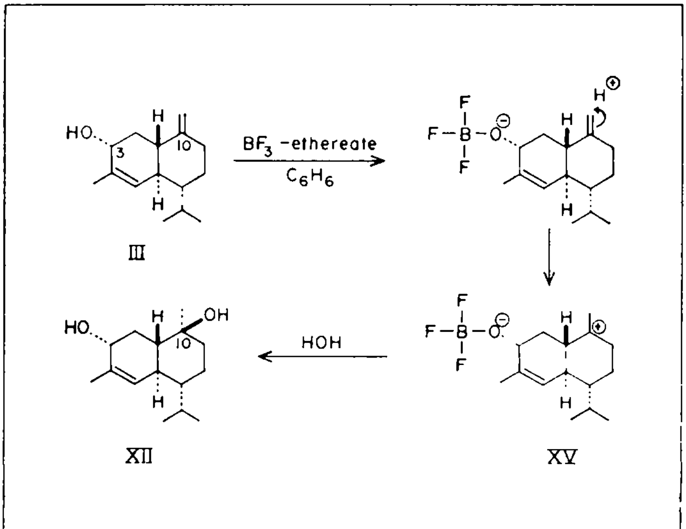


CHART II

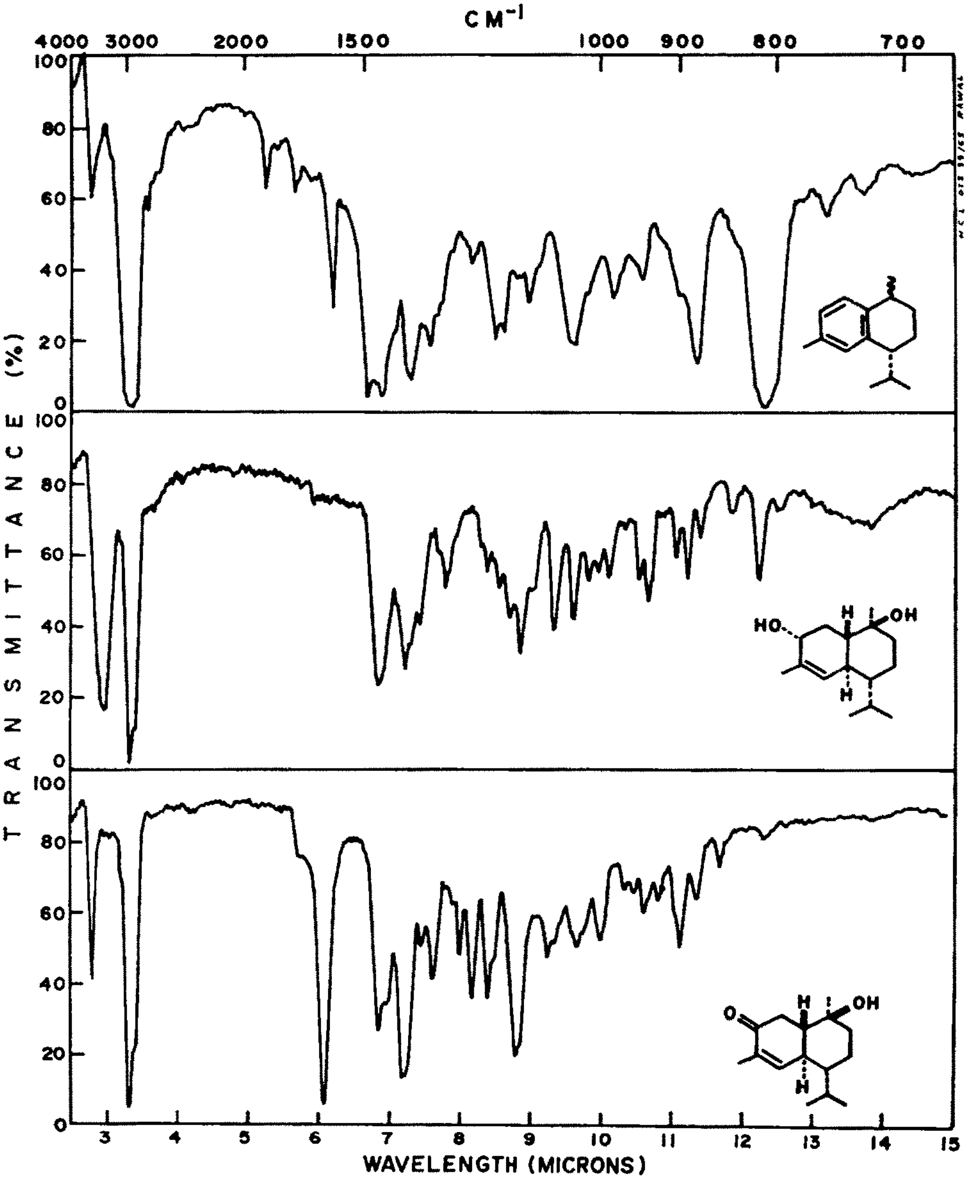


Fig. 1(a)

Mechanism for the formation of khusinodiol from khusinol

The sequence of reactions depicted in Chart II appears to explain satisfactorily the formation of khusinodiol (XII). The attack of BF$_3$-ethereate on hydroxyl group of khusinol (III) would result in the elimination of a proton which protonates a methylene group of the exocyclic double bond thereby forming the carbonium ion intermediate (XV). Upon addition of water, the BF$_3$-group would then be replaced by H^+ while OH^- would enter the position at C_{10} carbon atom.

Such hydration reactions are not very well known in the terpenic compounds.

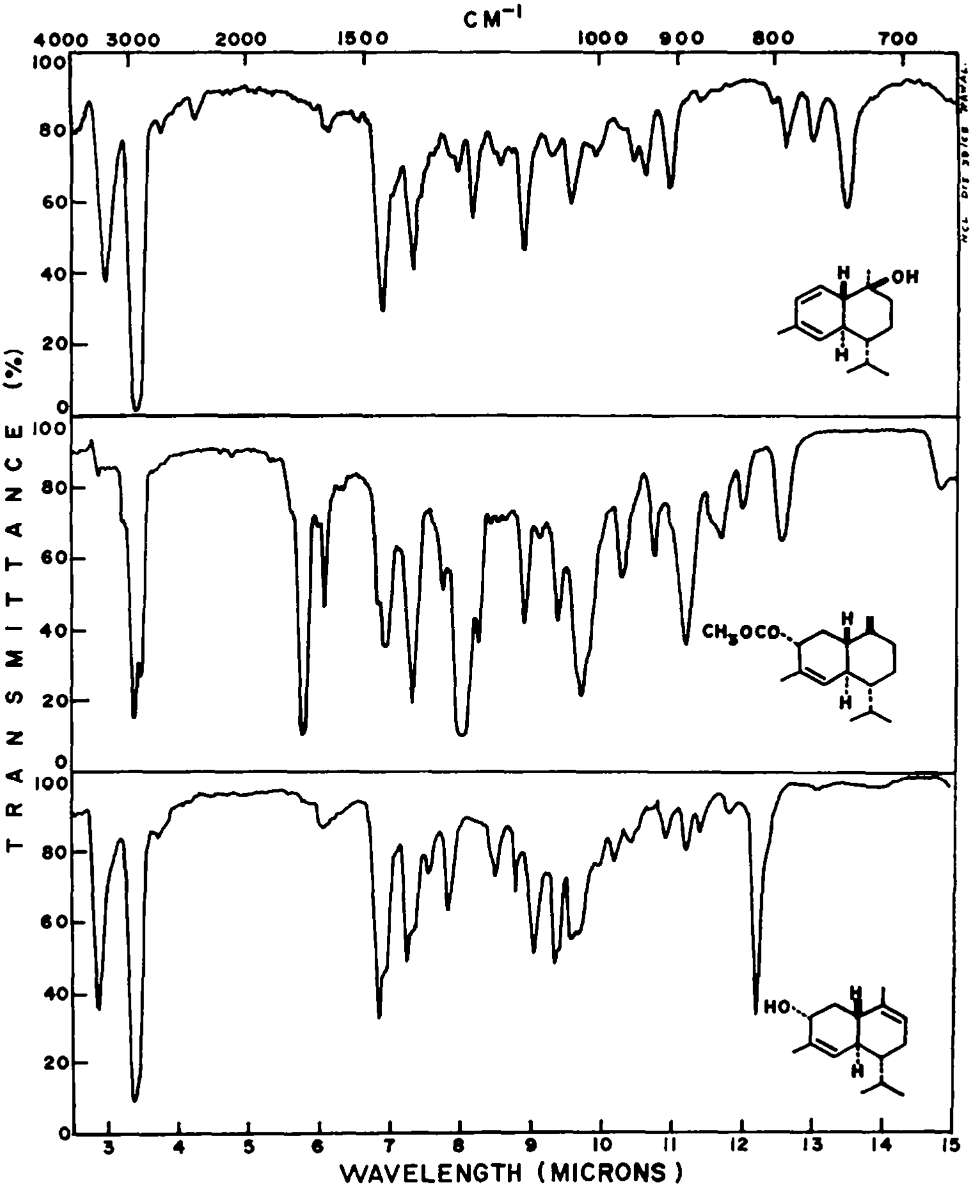


Fig. 1(b)

However, BF_3-catalysed hydration and dehydrogenation reactions of carotenes and related products have been thoroughly investigated.[16]

EXPERIMENTAL

The m.ps and b.ps are uncorrected. Rotations were taken in $CHCl_3$. IR and UV spectra were recorded on Perkin-Elmer (Model 137b) Infracord and DK-2 ratio recording spectrophotometers

[16] L. Wallcave, J. Leemann and L. Zechmeister, *Proc. N.A.S., USA.* 39, 604 (1953); L. Wallcave and L. Zechmeister, *J. Amer. Chem. Soc.* 75, 4495 (1953); F. J. Petracek and L. Zechmeister, *Ibid.* 78, 3188 (1956).

respectively by Gopinath and Deshpande. GLC analyses were carried out on a Griffin and George VPC apparatus MKIIA by Dr. Ghatge and colleagues. NMR spectra were taken on a 60 mc Varian instrument in CCl_4 solution with TMS as internal standard by Dr. Nair and colleagues. Microanalyses were carried out in the microanalysis section by Pansare and colleagues.

Reactions of BF_3*-ethereate on khusinol* (III). To a solution of khusinol (20 g) in dry benzene (50 ml), freshly distilled BF_3-ethereate (16 ml) was added dropwise during ½ hr at room temp-with stirring. The dark red reaction mixture was allowed to stand at room temp for 30 min and was poured into ice-water. Benzene layer was separated and the aqueous layer extracted with ether. The combined extract was washed with water and dried. Removal of solvent gave a residue (20 g), which was chromatographed over neutral alumina (grade III, 600 g) and eluted as follows:

Fr.	Solvent	Vol (ml)	Wt (g)	Remarks
1	Pet. ether	500	4.5	Mobil liquid
2	Benzene	1000	10.9	Viscous material
3	Ether	1000	3.8	Crystalline solid

Isolation of the hydrocarbon (I). The combined petroleum ether fraction (13 g from 3 batches) was rechromatographed on alumina (grade II, 650 g). Pet. ether eluted fraction (3 g) of this chromatography was found to be a mixture of hydrocarbons (VPC and TLC) which was further chromatographed (silica gel impregnated with $AgNO_3$, 150 g) and 21 fractions (5 ml each) with pet. ether were collected. Fractions 5–10 were combined on the basis of VPC and TLC ($AgNO_3$ impregnated silica gel plate using 5% benzene in pet. ether as the solvent phase). The pure hydrocarbon (0·9 g) so obtained was distilled *in vacuo* over Na. It had the following properties, b.p. 110° (bath)/1 mm, n_D^{29} 1·5180, $(\alpha)_D$ +82·58° (*c*, 3·26). VPC analysis gave single peak and TLC analysis showed single spot. IR spectrum (Fig. 1 in 0·01 mm liquid cell) showed bands at: 1887, 1754, 1613, 1493, 1449, 1365, 1313, 1220, 1176, 1157, 1111, 1042, 993, 943, 901, 882, 813, 757 cm^{-1}. (Found: C, 88·10; H, 10·70. $C_{15}H_{22}$ requires: C, 89·04; H, 10·96%.)

Dehydrogenation of the hydrocarbon (I). The hydrocarbon (0·1 g) was dehydrogenated with Se (50 mg) at 280–290° for 18 hr in N_2 atm. The dehydrogenated product was extracted with pet. ether and filtered through a column of alumina (grade I, 10 g) and the column was eluted with pet. ether. The hydrocarbon so obtained gave a complex with s-trinitrobenzene, which after recrystallization from EtOH had m.p. 110°. Mixed m.p. with authentic cadalene-TNB adduct remained undepressed.

Khusinodiol (II). The crystalline substance (12 g, from 3 batches) obtained from ether fraction of the chromatography was crystallized (twice) from pet. ether–ether (1:1) and further purified by sublimation at 130–140° (bath)/1 mm to give the pure khusinodiol (10 g), m.p. 133°, $(\alpha)_D$ +23·81° (*c*, 1·47). TLC analysis (solvent phase 15% ethylacetate in benzene) showed single spot. IR spectrum (Fig. 1 in nujol) bands at: 3500, 3350, 1379, 1363, 1333, 1274, 1190, 1170, 1145, 1126, 1070, 1042, 1015, 1002 990, 946, 935, 905, 892, 877, 844 and 817 cm^{-1}. (Found: C, 75·54; H, 11·39. $C_{15}H_{26}O_2$ requires: C, 75·63; H, 10·92%.)

Khusinodiol monoacetate (IV). Khusinodiol (2 g) was dissolved in anhydrous pyridine (10 ml) and acetic anhydride (2 ml) was added. The reaction mixture was allowed to stand overnight at room temp. The crude diol monoacetate (1·9 g) obtained by working up in the usual way was chromatographed on alumina (grade III, 100 g). Fractions eluted with a mixture of pet. ether and benzene (1:1) gave a crystalline monoacetate which on crystallization from pet. ether gave the pure diol monoacetate (1·2 g), m.p. 55°, $(\alpha)_D$ −42° (*c*, 2·65). IR spectrum (in nujol) bands at: 3500, 1750, 1333, 1299, 1230, 1170, 1124, 1091, 1064, 1031, 980, 971, 952, 935, 921, 874, 841, 820, 800 and 720 cm^{-1}. (Found: C, 72·78; H, 10·51. $C_{17}H_{28}O_3$ requires: C, 72·82; H, 10·06%.)

Oxidation of khusinodiol (II) *to the keto-alcohol* (V). Khusinodiol (0·5 g) was dissolved in dry acetone (50 ml) and 8N-H_2SO_4-CrO_3 reagent (Jones' reagent) was added slowly to a stirring solution till persistant orange colour was obtained. After 15 min the contents were poured into water (250 ml) and extracted with ether. The ether layer was washed initially with 5% $NaHCO_3$ aq and then with water and dried. After removal of solvent, the oxidation product on chromatography on alumina (grade III, 1:30) gave the keto alcohol (0·35 g) on elution with benzene. It was further purified by sublimation at 100° (bath)/1 mm. The keto monol (V) had the following properties, m.p. 90°, $(\alpha)_D$

+163·2° (*c*, 2·15); UV absorption, λ_{max} 236 mμ, ε_{max} 14640. IR spectrum (Fig. 1 in nujol), bands at: 3500, 1660, 1420, 1342, 1316, 1250, 1222, 1190, 1136, 1081, 1033, 1000, 965, 957, 943, 925, 901, 882 and 856 cm^{-1}. (Found: C, 76·32; H, 10·34. $C_{15}H_{24}O_2$ requires: C, 76·28; H, 10·17%.)

Partial tosylation of khusinodiol (II) *to mono tosyl derivative* (VI). Khusinodiol (5 g) was dissolved in dry pyridine (25 ml) and freshly crystallized *p*-toluenesulphonyl chloride (7 g) in dry pyridine (20 ml) was added. The mixture was kept at room temp for 48 hr. It was worked up in the usual way to obtain the crude mono tosylate (5·5 g).

LAH *reduction of the monotosylate* (VI) *to the diene monol* (VII). The crude monotosyl derivative (5·5 g) was dissolved in dry ether (50 ml) and added slowly to a slurry of LAH (1·5 g) in dry ether (100 ml) at 0°. Refluxing was carried out for 10 hr. The excess of LAH was decomposed with moist ether and finally with water. The product was isolated in the usual way and showed two spots on $AgNO_3$-impregnated silica gel plate using 7% ethyl acetate in benzene as a solvent phase. The reaction product (4·5 g) was chromatographed ($AgNO_3$-impregnated silica gel, 675 g) and eluted as follows:

Fr.	Solvent	Vol. of solvent collected ml.	Wt. of the material g.	Remarks
1–3	Benzene	3 × 50	—	mixture
4–6	Ethylacetate (5%) in benzene	2 × 10	—	mixture
7–10	Ethyl acetate (5%) in benzene	4 × 10	1.2	dienemonol

The last fraction was purified by crystallization from pet. ether followed by sublimation at 95° (bath)/0·15 mm. The diene monol (VII, 0·95 g), single spot on TLC, had the following properties, m.p. 109°, $(\alpha)_D$ +187° (*c*, 2·635). UV absortion: λ_{max} 260 mμ, ε_{max} 2606. IR spectrum (Fig. 1 in nujol) bands at: 3340, 1260, 1227, 1170, 1124, 1075, 1040, 1010, 956, 943, 912, 794, 764 and 743 cm^{-1}. (Found: C, 81·30; H, 11·20. $C_{15}H_{24}O$ requires: C, 81·76; H, 10·98%.)

Partial hydrogenation of diene monol (VII) *to* (+)-α-*cadinol* (VIII). A solution of diene monol (0·13 g) in EtOH (25 ml) was partially hydrogenated over pre-reduced Pd-C (50 mg, 5%) until the absorption corresponded to one mole of H_2 (13·2 ml at NTP). After filtering off the catalyst the filtrate afforded the dihydroproduct, (+)-α-cadinol (100 mg), which after purification by chromatography on alumina (grade III, 10 g), crystallization from pet. ether and sublimation at 75° (bath)/ 0·15 mm had m.p. 71–74°, $(\alpha)_D$+64° (*c*, 2·936). IR spectrum (in nujol) bands at: 3400, 1285, 1250, 1124, 1050, 1015, 952, 939, 926, 823, 797 and 785 cm^{-1}. (Found: C, 80·23; H, 11·66. $C_{15}H_{26}O$ requires: C, 81·02; H, 11·79%.)

Dehydration of khusinodiol monoacetate (IV) *and separation of khusinol acetate* (IX) *and isokhusinol acetate* (X). Khusinodiol monoacetate (1·1 g) was dissolved in a mixture of pyridine and benzene (2:1, 10 ml) and a solution of $POCl_3$ (2 ml) in benzene (3 ml) was added dropwise under stirring at room temp. The reaction was initiated by heating the mixture slowly to 60–65° and was kept at that temp for further 30 min under vigorous stirring. The mixture was then cooled, poured on crushed ice and worked up in the usual manner. The dehydrated product (1·1 g) was passed over a column of alumina (grade III, 36 g) and eluted with pet. ether. It showed two distinct spots on TLC analysis (silica gel-$AgNO_3$ plate, solvent-benzene). The dehydration product (1·1 g) was chromatographed (silica gel-$AgNO_3$ column, 1:50) to separate the two isomers. The chromatography details are given below:

Fr.	Solvent	Vol. (ml)	Wt (g)	Remarks
1–3	Benzene	3 × 5	0·130	Isokhusinol acetate
4–5	Benzene	2 × 5	0·040	
6	Benzene	1 × 5	—	mixture
7–10	Benzene	4 × 5	0·91	khusinol acetate.

Khysinol acetate (IX). Fractions 7–10 were combined together on the basis of VPC and TLC. It was purified by distillation *in vacuo*, b.p. 150° (bath)/0·5 mm, n_D^{20} 1·4994; $(\alpha)_D$ −157·3° (*c*, 2·67) and was identified as khusinol acetate by comparable physical properties and superimposable IR spectrum (Fig. 1, liquid film) with bands at: 1739, 1640, 1290, 1250, 1212, 1124, 1066, 1031, 971, 934, 893, 855, 833 and 796 cm^{-1}. On hydrolysis it gave khusinol (III), m.p. 85–86°, $(\alpha)_D$ −164·7° (*c*, 7·31).

Isokhusinol acetate (X). Fractions 1–5, which showed single spot on TLC, were mixed together. On evapoaration of solvent isokhusinol acetate was obtained which was purified by distillation *in vacuo*, b.p. 140–145° (bath)/0·5 mm, n_D^{20} 1·4990, $(\alpha)_D$ −33·64° (*c*, 2·18). Its IR spectrum showed bands at: 1742, 1250, 1130, 1070, 1031, 975, 934, 873, 847 and 816 cm^{-1}. (Found: C, 77·73; H, 10·13. $C_{17}H_{26}O_2$ requires: C, 77·82; H, 9·99%.)

Hydrolysis of isokhusinol acetate (X) *to isokhusinol* (XI). Isokhusinol acetate (90 mg) was dissolved in alcoholic-KOH solution (10%, 20 ml) and refluxed over water bath for 4 hr. The contents after cooling were poured on crushed ice and extracted with ether. The ether layer was washed with water and dried. Removal of solvent gave crude crystalline alcohol (70 mg) which was purified by crystallization from pet. ether followed by sublimation at 90° (bath)/0·2 mm. Isokhusinol (60 mg) had m.p. 87–88°, $(\alpha)_D$ +22·2° (*c*, 1·125). IR spectrum (Fig. 1, in nujol), bands at: 3470, 1460, 1440, 1380, 1361, 1325, 1274, 1176, 1136, 1110, 1070, 1042, 1031, 980, 961, 912, 893, 877 and 820 cm^{-1}. (Found: C, 81·30; H, 11·10. $C_{15}H_{24}O$ requires: C, 81·02; H, 11·79%.)