Tetrahedron, 1963, Vol. 19, pp. 233 to 239. Pergamon Press Ltd. Printed in Northern Ireland

TERPENOIDS—XXXVI

THE STRUCTURE OF KHUSINOL A NEW SESQUITERPENE ALCOHOL FROM VETIVER OIL*

A. A. Rao, K. L. Surve, K. K. Chakravarti and S. C. Bhattacharyya
National Chemical Laboratory, Poona

(*Received* 22 *May* 1962)

Abstract—Khusinol, a new crystalline secondary sesquiterpene alcohol, isolated from North Indian vetiver oil (*Vetiveria zizaniodes*, Linn.) is shown to have the absolute configuration represented by the structure XX on the basis of degradative experiments and its conversion to $(-)$-γ-cadinene under mild conditions. It belongs to the unusual antipodal group of cadinenes. γ_1-Cadinene (XXI) isolated from Malabar lemongrass oil has also been shown to belong to the same antipodal group.

THE laevorotatory vetiver oil (*Vetiveria zizaniodes*, Linn.) from Bharatpur and Biswan area of North India on chromotography over neutral alumina gave a crystalline secondary alcohol, $C_{15}H_{24}O$, m.p. 87°, as a major constituent. We propose to name it as 'khusinol', so as to distinguish it from the primary alcohol khusol, m.p. 101–102°, isolated from vetiver oil[1] and characterized by Bhattacharyya *et al.*[2] Evidence put forward in the present communication shows that the gross structure of khusinol is represented by the structure I and its absolute configuration by structure XX. It belongs to the unusual antipodal group of cadinenes and is of considerable interest from a biogenetic point of view. Khusinol also appears to be the first secondary alcohol of the cadinane group so far reported.

The IR spectrum of khusinol exhibits absorption bands (Fig. 1) at 3400, 1074 (hydroxyl group), 909, 898 and 1642 (terminal methylene group), 797 and 1667 (trisubstituted double bond) and 1340 and 1372 (isopropyl group) cm^{-1}. On hydrogenation with Adams catalyst in glacial acetic acid it absorbed two moles of hydrogen to furnish tetrahydrokhusinol (III), $C_{15}H_{28}O$, m.p. 93–94°. Perbenzioc acid titrations also showed the presence of two double bonds in khusinol. Hence khusinol is a bicyclic compound. It did not show any UV absorption maximum indicating absence of conjugation. Khusinol easily formed a liquid acetate, $C_{17}H_{26}O_2$, on treatment with acetic anhydride and pyridine at room temperature. On dehydrogenation with selenium at 280–286°, khusinol afforded cadalene in an excellent yield. It is, therefore, a cadinenic sesquiterpene alcohol. On ozonolysis it gave formaldehyde as the only volatile fragment and no acetone was formed. The non-volatile portion gave tests for methyl ketone and aldehyde function.

Khusinol, on chromic acid oxidation in acetic acid, gave an $\alpha\beta$-unsaturated ketone (IV), $C_{15}H_{22}O$ (λ max 243 mμ, log ϵ, 4·01; IR bands at 1653 and 1600 cm^{-1}). On partial hydrogenation with palladized carbon in alcohol it absorbed only one mole of hydrogen to give dihydrokhusinol (II), $C_{15}H_{26}O$, m.p. 111°. Its IR spectrum indicated

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

[1] N. L. Zutshi and Sadgopal, *Perfum. Essent. Oil Rec.* **47**, 88 (1956).

[2] S. N. Dhingra, D. R. Dhingra and S. C. Bhattacharyya, *Perfum. Essent. Oil Rec.* **47**, 350 (1956).

the presence of trisubstituted double bond (bands at 800 and 1665 cm^{-1}) and absence of bands due to methylenic double bond. Dihydrokhusinol on chromic acid oxidation in acetic acid furnished a crystalline $\alpha\beta$-unsaturated ketone (V), $C_{15}H_{24}O$, m.p. 96–97°. Its UV absorption (λ max 233 mμ, log ϵ, 4·14) and IR specrtum (bands at 1647 and 1613 cm^{-1}) indicated that the hydroxyl group in dihydrokhusinol was allylic to the trisubstituted double bond. On complete hydrogenation, dihydrokhusinol absorbed one mole of hydrogen and furnished tetrahydrokhusinol (III) which on chromic acid oxidation gave a liquid saturated ketone (VI), $C_{15}H_{26}O$; IR band at 1704 cm^{-1} indicated the keto group on a six-membered ring. Oxidation of khusinol with activated manganese dioxide yielded the ketone IV in unsatisfactory yield. Kuhn-Roth estimations of khusinol and dihydrokhusinol (1·75 and 2·22 respectively) showed a definite rise in the C-CH_3 groups indicating that the methylenic double bond was not in the C_7-isopropyl side-chain.

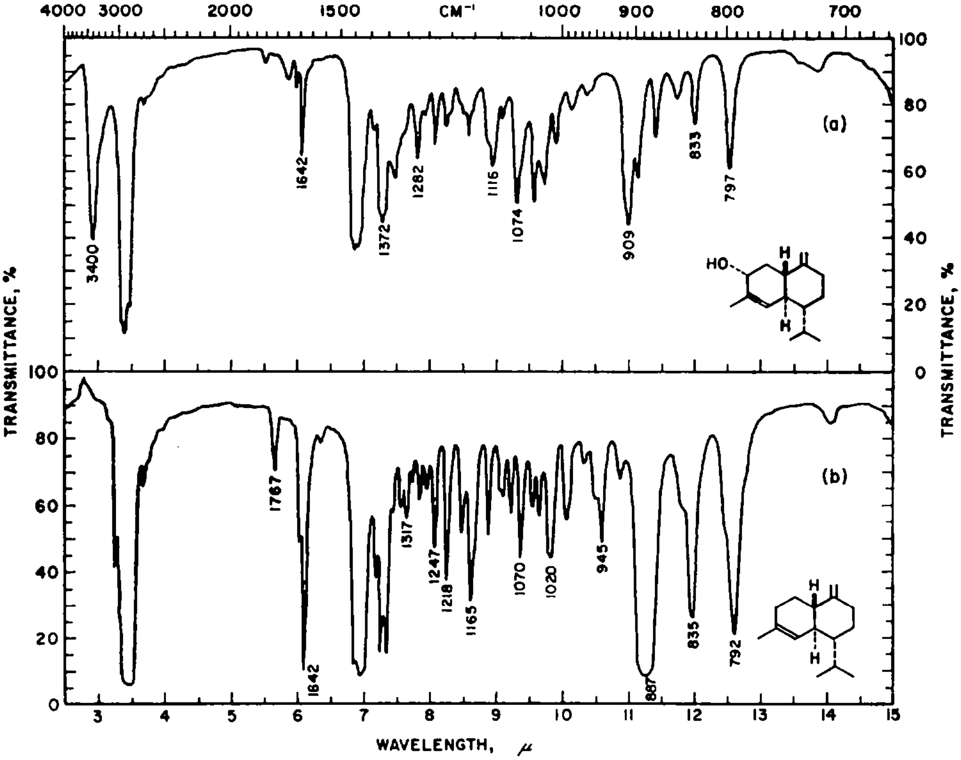

FIG. 1. Infra-red spectra of (a) khusinol (in Nujol). (b) (−)-γ-Cadinene (in liquid cell, 0·1 mm) from khusinol.

In order to determine the position of the secondary hydroxyl group, the saturated ketone (VI) obtained by chromic acid oxidation of tetrahydrokhusinol (III) was treated with methyl magnesium iodide to yield the carbinol (VII) which of dehydrogenation with selenium afforded 7-methyl-cadalene (VIII).

Additional proof for the position of the trisubstituted double bond was obtained by the labelling method of Campbell and Soffer.[3] Epoxy alcohol (IX) prepared by the

[3] W. P. Campbell and M. D. Soffer, *J. Amer. Chem. Soc.* **64**, 417 (1942).

action of perbenzoic acid of dihydrokhusinol (II) was treated with methyl magnesium iodide. The diol (X) thus obtained on subsequent dehydrogenation with selenium afforded 1,2,5-trimethylnaphthalene (XI), the isopropyl group at C_7 being eliminated during dehydrogenation.[4] These reactions conclusively prove the gross structure (I) for khusinol.

With a view to elucidating the absolute configuration of assymmetric centres of khusinol, it was converted to its tosylderivative by treating with tosylchloride in pyridine solution at room temperature for 80 hours in a yield of 80%. Attempts to increase the yield by heating and shaking at higher temperatures gave rise to secondary products. Similar attempts to isolate the tosyl derivative in a pure form by chromatography on alumina resulted in decomposition of the tosylate. The tosylate on reduction with lithium aluminium hydride and subsequent chromatography gave a hydrocarbon, $C_{15}H_{24}$ (XII) in good yield. Its IR spectrum (Fig. 1) and physicochemical constants were identical with those of (+)-γ-cadinene (XIII), $[\alpha]_D$ + 148°, isolated by Pliva *et al.*[5] from citronella oil. However, its specific rotation (−153°) clearly indicated that the hydrocarbon (XII) obtained from khusinol was the optical antipode of (+)-γ-cadinene (XIII). To further confirm the antipodal nature of the hydrocarbon (XII), it was converted to its crystalline dihydrochloride (XIV). Its melting point, 117·5°, was identical with that of normal (−) cadinene-dihydrochloride (XV), m.p. 118°, but its specific rotation (+36·2°) was equal but opposite in sign to that of normal cadinene-dihydrochloride (−36°).

Mixed melting point of (+) cadinene dihydrochloride (XIV) from khusinol with an authentic sample of (−)-cadinene dihydrochloride (XV)* showed depression (102°) which is in accordance with expectation, since (±)-cadinene-dihydrochloride, m.p. 105–106°, has been obtained from optically inactive δ-cadinene[6,7] and has also been synthesized.[8]

Absolute configuration of cadinenes and cadinols yielding (−)-cadinene dihydrochloride have been determined on the basis of X-ray diffraction measurement of (−)-cadinene dihydrochloride[9] (XIV) and also by determining the absolute configuration at C_7 by isolating D-(+)-isopropyl succinic acid (XVI)[10] as an ultimate product of oxidative degradation of β-cadinene. Same conclusion has been arrived at by comparative study of the rotatory dispersion curves of the ketones(XVII and XVIII) obtained from α-cadinol[11] with that of the ketone[12] (XIX) whose absolute configuration is known. Consequently, (−)-γ-cadinene from khusinol and (+)-cadinene dihydrochloride obtained from it are represented by the antipodal configurations (XII and XIV). The O.R.D. curves† of (+)-cadinene-dihydrochloride and (−)-cadinene dihydrochloride

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* We are thankful to Dr. Sukhdev for the sample.

† We are thankful to Prof. W. Klyne for determining the O.R.D. curves.

[4] M. D. Soffer, M. Brey and J. Fournier, *J. Amer. Chem. Soc.* **81**, 1678 (1959).

[5] V. Herout, T. Kolos and J. Pliva, *Chem. Listy* **47**, 440 (1953); *Coll. Trav. Chim. Tchecosl.* **18**, 886 (1953).

[6] R. P. Hildebrand and M. D. Sutherland, *Austr. J. Chem.* **12**, 678 (1959).

[7] R. O. Hellyer and H. H. G. McKern, *Austr. J. Chem.* **9**, 547 (1956).

[8] M. V. R. Koteshwara Rao, G. S. Krishna Rao and Sukh Dev, *Tetrahedron letters* No. 27, 27, (1960).

[9] F. Hanic, *Chem. Listy* **52**, 165 (1958).

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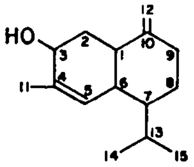
[12] D. Marshall and C. Djerassi, *J. Amer. Chem. Soc.* **80**, 3986 (1958).



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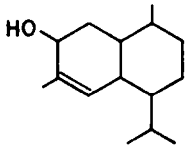

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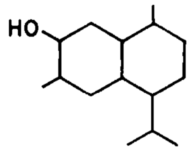

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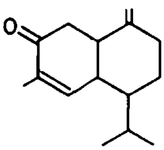

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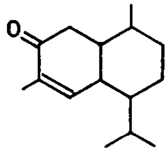

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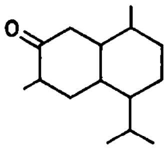

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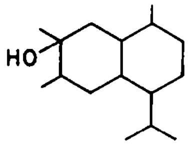

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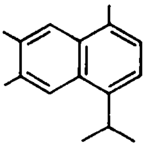

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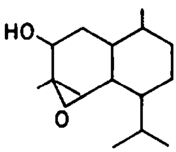

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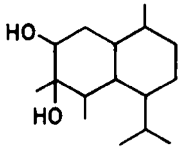

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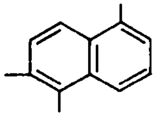

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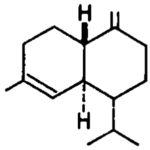

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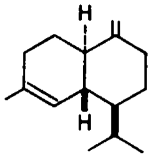

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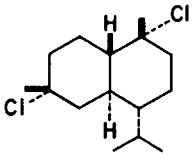

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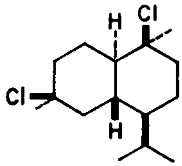

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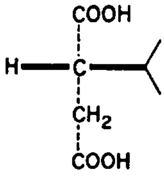

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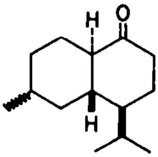

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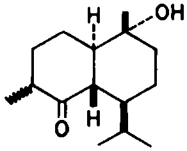

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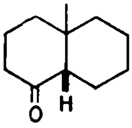

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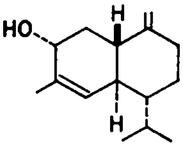

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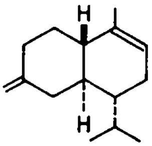

XXI

also show enantiomeric relationship. Khusinol, therefore, can be represented by the absolute configuration XX where the hydroxyl group is assigned α-equatorial orientation from its ease of esterification.

A survey of literature indicates that (+)-cadinene dihydrochloride had been previously obtained by Gardner[13,14] from a sesquiterpene fraction. He also proved from a study of the melting point curves that (+)-cadinene dihydrochloride obtained by him was the optical antipode of (—)-cadinene dihydrochloride usually obtained from cadinenic compounds.

Previously, γ_1-cadinene[15,16] has been isolated in this laboratory from Malabar lemongrass oil and its structure elucidated. It also gives cadinene dihydrochloride, m.p. 118°. Its specific rotation which was not determined at that time has now been found to be +36·8°. It does not depress the melting point of (+)-cadinene dihydrochloride obtained from (—)-γ-cadinene, but depresses the melting point of (—)-cadinene dihydrochloride.

γ_1-Cadinene, therefore, also belongs to the antipodal group and is assigned the absolute configuration (XXI).

Khusinol may be identical with cussol isolated and preliminarily examined by Zutshi and Sadgopal.[17]

EXPERIMENTAL

All mp's and bp's are uncorrected. Rotations were measured in chloroform. UV spectra were taken in 95% alcohol on Beckman DK_2 recording spectrophotometer. IR spectra were determined with Perkin Elmer model 221 and 137 infracord spectrophotometer.

Vetiver oil was obtained from reliable suppliers at Kannauj, contacted through Government agencies.

Isolation of khusinol (I). Vetiver oil (400 g) was chromatographed on neutral alumina (grade II, 6 kg) and eluted successively with pet ether (15 l.); ether (14 l.) and alcohol (10 l.). The product (250 g) obtained by elution with ether was rechromatographed on neutral alumina (grade II, 3·3 kg). The viscous pet ether eluate deposited crystals of khusinol on keeping at 0°. The crystals (20% from Bharatpur oil and 30% from Biswan oil) were filtered off and recrystallized from pet ether, m.p. 87°; $[\alpha]_D^{25}$ 174·4° (*c*, 5·03) (Found: C, 81·03; H, 11·1. $C_{15}H_{24}O$ requires: C, 81·76; H, 10·98%).

IR spectrum (in Nujol): Bands at 3400, 1709, 1667, 1642, 1372, 1340, 1282, 1241, 1215, 1166, 1116, 1074, 1045, 1029, 1010, 909, 898, 877, 851, 838 and 797 cm^{-1}.

Khusinol acetate. Khusinol (0·5 g) was treated with pyridine (50 ml) and acetic anhydride (7 ml) at room temp for 24 h. Contents were poured into crushed ice and processed in the usual way. The crude acetate (0·641 g) was chromatographed on alumina (grade II, 20 g) and the pet ether eluate after evaporation of solvent was distilled (0·503 g), b.p. 150° (bath) 0·5 mm, n_D^{28} 1·4999; $[\alpha]_D^{28}$ —168·4° (*c*, 6·855) (Found: C, 78·0; H, 10·1. $C_{17}H_{26}O_2$ requires: C, 77·82; H, 9·99%). IR bands at: 1715, 1625, 1220, 1050, 890, 795 cm^{-1}.

Dehydrogenation of khusinol (I). Khusinol (0·5 g) was heated with selenium powder (1 g) at 280–286° for 17 hr in nitrogen atmosphere. The dehydrogenated product was extracted with ether and filtered to give 0·31 g of dehydrogenation product. Cadalene content was about 90% on the basis of UV spectrum. It readily formed cadalene picrate, m.p. and mixed m.p. with an authentic specimen was 115°.

Ozonolysis of khusinol (I). A stream of dry ozonized oxygen was passed through a solution of khusinol (0·146 g) in dry chloroform (20 ml) for 3 hr at 0°. The ozonized solution was steam distilled and the distillate containing chloroform was treated with dimedone solution (0·52 g in 200 ml water).

[13] R. Gardner, *J. Soc. Chem. Ind.* (*Trans*) **50**, 141 (1931).

[14] A. J. Birch, *J. Chem. Soc.* 715 (1953).

[15] K. K. Chakravarti and S. C. Bhattacharyya, *Perf. & Ess. Oil Rec.* **46**, 365 (1955).

[16] B. B. Ghatge, R. K. Razdan and S. C. Bhattacharyya, *Perf. & Ess. Oil Rec.* **47**, 157 (1956).

[17] N. L. Zutshi and Sadgopal, *Perf. & Ess. Oil. Rec.* **48**, 333 (1957).

Chloroform was removed by distillation and on cooling formaldimethane separated, which was filtered and dried to constant weight (m.p. and mixed m.p. 189°; 0·052 g, 26·83% of theory). The steam distillate gave negative iodoform test. The decomposed ozonide was extracted with ether and solvent evaporated. The non-volatile residue gave positive iodoform test in dioxan and reduced Fehling's solution.

Ketone (IV) *from khusinol.* A solution of chromium trioxide (2·8 g) in minimum amount of water was added to a solution of khusinol (5·2 g) dissolved in glacial acetic acid (15 ml) under cooling and shaking during 10 min, followed by heating on a water bath for 1 hr and was then left overnight at room temp. Reaction mixture was diluted with water and extracted with ether. Ether extract was separated into acidic (0·15 g) and neutral fractions (4·2 g). The neutral product after chromatography on alumina (grade II, 80 g) gave the pure ketone (IV, 0·45 g) on elution with pet ether, b.p. 155–160° (bath)/2·5 mm; n_D^{27} 1·5315; $[\alpha]_D^{25}$ +49·86° (*c*, 5·234) (Found: C, 81·79; H, 10·25. $C_{15}H_{22}O$ requires: C, 82·51; H, 10·16%). UV spectrum: λ max 243 mμ, log ϵ, 4·01. IR bands at: 1653, 1600, 1422, 1376, 1361, 1295, 1266, 1248, 1232, 1134, 1106, 1070, 1042, 1020, 896, 875, 859, 795 cm^{-1}.

Dihydrokhusinol (II). Khusinol (5·52 g) was hydrogenated at room temp and atm. press. in ethanol (25 ml) in presence of 8% palladized carbon (0·6 g). Hydrogen equivalent to one double bond was absorbed in 3½ hr, after which the absorption became very slow. Hydrogenation was stopped at this stage. Catalyst was filtered off and the filtrate evaporated, the residue (5·8 g) chromatographed over alumina (grade II, 200 g) and the column eluted successively with pet ether (fractions 1 to 4), pet ether–benzene (3:1; fractions 5 to 12) and finally with ether. Fraction 3 to 12 which showed identical IR spectra, were all solid and were sublimed separately. Melting points ranged from 106° to 111° due to presence of isomers formed during hydrogenation. Fraction No. 8 used as an analytical sample had m.p. 111°; $[\alpha]_D^{25}$ +12·15° (Found: C, 80·95; H, 12·1. $C_{15}H_{26}O$ requires: C, 81·02; H, 11·79%). IR (in Nujol) bands at: 3300, 1701, 1665, 1289, 1263, 1190, 1157, 1117, 1099, 1053, 1036, 1008, 973, 897, 889, 869, 826, 800, 795 cm^{-1}.

Ketone (V) *from dihydrokhusinol.* Chromium trioxide (0·3 g) dissolved in minimum amount of water was added to a solution of dihydrokhusinol (0·48 g, m.p. 108–110°) in glacial acetic acid (8 ml) under cooling and shaking during 5 min. The reaction mixture was heated on a water bath for 1 hr and was left overnight at room temp and the contents diluted with water and extracted repeatedly with ether. The ether layer was washed successively with water, sodium bicarbonate solution (8%) and finally with water and dried. After removal of solvent, the residue (0·496 g) was chromatographed over alumina (grade II, 15 g). The pure ketone (V) was eluted with pet ether–benzene (1:1), m.p. 92°, which after careful sublimations was 96–97°; $[\alpha]_D^{26}$ +48·37° (*c*, 1·375) (Found: C, 81·8; H, 10·91. $C_{15}H_{24}O$ requires: C, 81·76; H, 10·98%). UV spectrum: λ max 233 mμ, log ϵ, 4·14. IR (in Nujol) bands at: 1647, 1613, 1429, 1377, 1366, 1304, 1274, 1227, 1175, 1089, 1056, 1026, 1009, 983, 923, 90s, 893, 884, 873, 858, 821, 799 cm^{-1}.

Tetrahydrokhusinol (III). A solution of dihydrokhusinol (m.p. 107–111°, 3·36 g) in glacial acetic acid (25 ml) was hydrogenated at room temp and atm. press. in the presence of Adams catalyst (0·014 g). The hydrogenation was complete after the absorption of 350 ml hydrogen corresponding to 0·85 mole hydrogen during 5 hr. The catalyst was filtered off and the filtrate neutralized with potassium hydroxide solution (10%) and the hydrogenated product taken up in ether. The ether layer was washed till neutral and dried. The tetrahydroproduct (3·22 g) was chromatographed over alumina (grade III, 100 g) and eluted with pet ether and pet ether–benzene (1:1) and sublimed to give tetrahydrokhusinol (III), m.p. 93–94°; $[\alpha]_D^{24}$, 20·84° (Found: C, 79·63; H, 12·46. $C_{15}H_{28}O$ requires: C, 80·29; H, 12·58%). IR (in Nujol) bands at: 3260, 1376, 1361, 1342, 1269, 1192, 1156, 1134, 1099, 1050, 1040, 960, 887, 860, 840, 825, 795 cm^{-1}. Some slightly lower melting fractions having nearly identical IR spectra were also obtained. This evidently was due to presence of isomers. A trace of hydrocarbon was also formed due to hydrogenolysis of the allylic hydroxyl group.

Ketone (VI) *from tetrahydrokhusinol.* A solution of tetrahydrokhusinol (4 g) in glacial acetic acid (50 ml) was oxidized with chromium trioxide (4 g) following the procedure described earlier. The ketone (VI) formed was purified by chromatography and distillation, b.p. 140–150° (bath)/3·4 mm; $[\alpha]_D^{24}$ +18·8° (*c*, 5·155); n_D^{24} 1·4849 (Found: C, 81·5; H, 11·9. $C_{15}H_{26}O$ requires: C, 81·02; H, 11·79%). IR bands at: 1704, 1453, 1418, 1377, 1361, 1326, 1290, 1266, 1225, 1200, 1186, 1168, 1136, 1120, 1111, 1083, 1063, 1042, 1018, 973, 940, 920, 905, 894, 873, 860, 825, 797 cm^{-1}.

Grignard reaction on tetrahydroketone and dehydrogenation of the carbinol (VII). The ethereal solution of tetrahydroketone (VI, 0·75 g) was added dropwise to methyl magnesium iodide prepared from magnesium (0·49 g) and methyl iodide (1·5 ml) in dry ether (10 ml) with cooling and stirring. The mixture was refluxed for 3 hr. Grignard complex was then decomposed by the addition of saturated ammonium chloride solution at 0°, extracted with ether, washed with water, dried and solvent evaporated when crude carbinol (0·87 g) was obtained. IR spectrum showed the presence of small amount of ketonic impurities which was removed by chromatography over alumina (grade II, 80 g) and elution with pet ether. A portion of the carbinol (0·19 g) eluted with pet ether–benzene (1:1) was heated with palladized carbon (30%, 0·1 g) at 300–330° for 20 hr in nitrogen atmosphere. The hydrogenated product was taken up in ether, washed with caustic soda solution (5%), water and dried, and ether evaporated. The residue (0·145 g) was chromatographed over alumina (grade II, 20 g) and eluted with pet ether to yield the hydrocarbon (0·11 g). It furnished 1,3,5 TNB derivative of 7-methyl cadalene (VII), m.p. 126° (Found: C, 62·5; H, 5·2; N, 10·0. $C_{22}H_{23}O_6N_3$ requires: C, 62·36; H, 5·45; N, 9·88%).

Epoxy alcohol (IX) *from dihydrokhusinol.* Dihydrokhusinol (1·7 g) dissolved in chloroform (5 ml) was treated with a chloroform solution of perbenzoic acid (120 ml, 0·25N) and kept at 0° for 16 hr. Chloroform solution was washed with bicarbonate, water and dried. Evaporation of solvent gave crude epoxy alcohol (IX, 1·86 g). IR bands at: 3280, 1700, 1263, 1214, 1111, 1089, 1010, 909, 872, 840, 826, 713 cm^{-1}.

Dehydrogenation of diol (X). A solution of the epoxy alcohol (1·86 g) in dry ether (10 ml) was added to methyl magnesium iodide prepared from magnesium (4·1 g) and methyl iodide (20 ml) in dry ether (30 ml) under cooling and stirring during 1 hr and then refluxed for 47 hr. Ethanol (20 ml) was added dropwise followed by cold dil. sulphuric acid. Contents were taken up in ether, washed with water till neutral and dried. On evaporation of solvent diol (X, 2·28 g) was obtained. It was mixed with selenium powder (4·2 g) and heated at 275–80° for 24 hr in nitrogen atmoshpere. The product was taken up in ether, concentrated and passed through alumina column (grade I, 30 g) to yield 1,2,5 -trimethylnaphthalene (1·24 g), UV spectrum: λ max 227 mμ, log ϵ 4·77, λ max 284 mμ, log ϵ 3·61. It gave a picrate which after two crystallizations from ethanol melted at 136–39°. Hydrocarbon (0·4386 g) was regenerated by passing the picrate through alumina column (grade I, 12 g) and TNB adduct was prepared, m.p. and mixed m.p. with an authentic sample was 160°. (Found: C, 59·75; H, 4·2; N, 11·5. $C_{19}H_{17}O_6N_3$ requires: C, 59·53; H, 4·47; N, 10·96%).

(−)-γ-*Cadinene* (XII). A mixture of khusinol (2 g) in dry pyridine (35 ml) and freshly crystallized *p*-toluene sulphonyl chloride (2 g) in dry pyridine (10 ml) was kept at room temp for 80 hr. Three such independent batches were then combined and poured into crushed ice and taken up in ether. Ether layer was washed successively with dilute hydrochloric acid, water, sodium bicarbonate solution and finally with water and dried. After evaporating the solvent crude tosylate (6·26 g) was obtained. The IR spectrum showed a small hydroxy peak (3300 cm^{-1}) and intense bands due to tosyl group (1603, 1500, 1186, 1170, 1095, 1050 cm^{-1}. The tosylate (6·26 g) in dry ether (25 ml) was added dropwise to a slurry of lithium aluminium hydride (2·12 g) in dry ether (50 ml) at 0° with stirring, which was continued for 30 min. The contents were then refluxed for 15 hr. The excess of lithium aluminium hydride was decomposed cautiously by the addition of moist ether and water. Ether layer was separated and the acqueous layer was extracted several times with ether. Combined ether extracts were washed with water till neutral, dried and ether evaporated. The residue (4·19 g) was chromatographed over alumina (grade I, 120 g) and the column eluted with pet ether to give (−)-γ-cadinene (2·5 g) which was distilled over sodium, b.p. 130–33° (bath)/4·3 mm; n_D^{28} 1·5083; d_D^{24} 0·9189; $[\alpha]_D^{24}$ −153° (*c*, 2·476) (Found: C, 88·22; H, 11·76. $C_{15}H_{24}$ requires: C, 88·16; H, 11·84%). IR bands at: 1767, 1665, 1642, 1391, 1379, 1362, 1332, 1317, 1285, 1268, 1247, 1218(s), 1187, 1165(s), 1130, 1102, 1089, 1070, 1050, 1040, 1020, 996, 969, 954, 945, 920, 887, 835, 792 cm^{-1}.

Dihydrochloride (XIV) *of* (−)-γ-*cadinene.* Dry gaseous hydrogen chloride was bubbled through ethereal solution of hydrocarbon (1·2 g in 75 ml) for 2 hr at −10° and left overnight at 0°. Solvent was removed at 40° under suction. On cooling, crystals deposited which after one crystallization from dry pet ether and ether (1:1) gave the dihydrochloride, m.p. 117·5°; $[\alpha]_D^{24}$ +36·27° (Found: Cl, 23·9. $C_{15}H_{24}Cl_2$ requires: Cl, 25·82%). Mixed m.p. with an authentic sample of canedine dihydrochloride (m.p. 118°, $[\alpha]_D^{24}$ −36°) was depressed to 102°.