Tetrahedron Vol. 24, pp. 3809 to 3827. Pergamon Press 1968. Printed in Great Britain

STUDIES IN SESQUITERPENES—XXIX

STRUCTURE OF HIMACHALENES*

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(*Received in the UK* 12 *September* 1967; *accepted for publication* 5 *December* 1967)

Abstract—α- and β-Himachalenes, the two major sesquiterpene components of the essential oil of Himalayan deodar (*Cedrus deodara*, Loud.) are shown to represent a new sesquiterpenoid carbon framework. Evidence is presented which establishes their gross structures.

THE essential oil from Himalayan deodar (*Cedrus deodara*, Loud.) is known[1] to contain two new sesquiterpene hydrocarbons, namely α- and β-himachalenes. From a preliminary investigation reported earlier,[1] it was suggested that these closely related hydrocarbons represent a new type in sesquiterpenoids and, the present work which describes the structure elucidation of these compounds,[2] confirms our previous contention.

By the application of GLC it was found that the previously reported[1] hydrocarbons were somewhat contaminated with each other. Table 1 records the physical properties of thoroughly purified samples.

TABLE 1. PHYSICAL CHARATERISTICS OF α- AND β-HIMACHALENES

	b.p./mm	n_D^{25}	d_4^{25}	M_D	$[\alpha]_D^{25}$ (CHCl$_3$)
α-Himachalene	93–94°/2	1·5082	0·9206	65·85	−192·3°
β-Himachalene	121–122°/4	1·5130	0·9330	65·71	+224·7°

Relationship of α- and β-himachalenes. Both hydrocarbons analysed for $C_{15}H_{24}$ and their molecular refractivity (Table 1) suggested these to be bicyclic containing two ethylenic linkages. Though, the observed molecular refractivity is rather lower† than the calculated value (66·13), their bicyclic nature was confirmed by estimating the number of ethylenic linkages. Both quantitative catalytic hydrogenation and percamphoric acid epoxidation revealed the presence of two double bonds in each of the hydrocarbons.

Both on interaction with hydrogen chloride in acetic acid yielded the same crystalline dihydrochloride (m.p. 118–119°), which readily passed into a monohydrochloride

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* Communication No. 1124, National Chemical Laboratory, Poona.

† Depression of molecular refractivity has been observed for medium ring-sized[3a] as well as for certain compounds having quaternary carbon atoms.[3b]

(m.p. 51–52°) on mere recrystallization from MeOH. This instability of the dihydrochloride is reflected in the measurement of its $[\alpha]_D$ in $CHCl_3$, which is clearly dependent (*vide* Experimental) on time, and the true value of its $[\alpha]_D$ ($-9{\cdot}25$) could be obtained only by extrapolation to zero time.

The IR spectra of tetrahydro-α- and tetrahydro-β-himachalenes (Fig. 1), though quite similar, show significant differences in the intensities of several bands in the fingerprint region. This is explained on the basis of formation of differing amounts of stereo-isomers during hydrogenation. The GLC of these products disclosed in each case at least two components; the component with the lower retention time being present to the extent of 66% in the case of tetrahydro-α-isomer and 15% in the β-isomer. The IR spectra and the physical constants of these products differ from those recorded for several known perhydro bicyclic sesquiterpene systems[4,5] and,

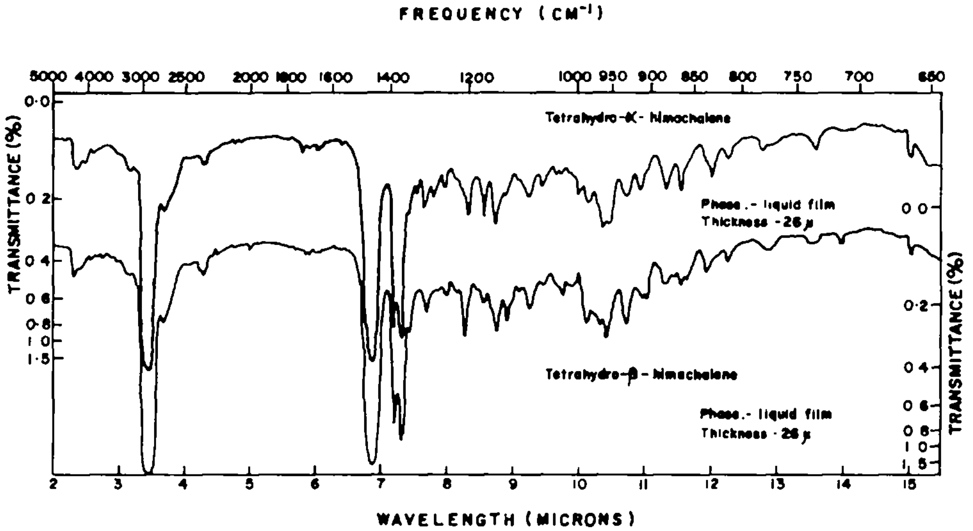

FIG. 1 IR Spectra of tetrahydrohimachalenes

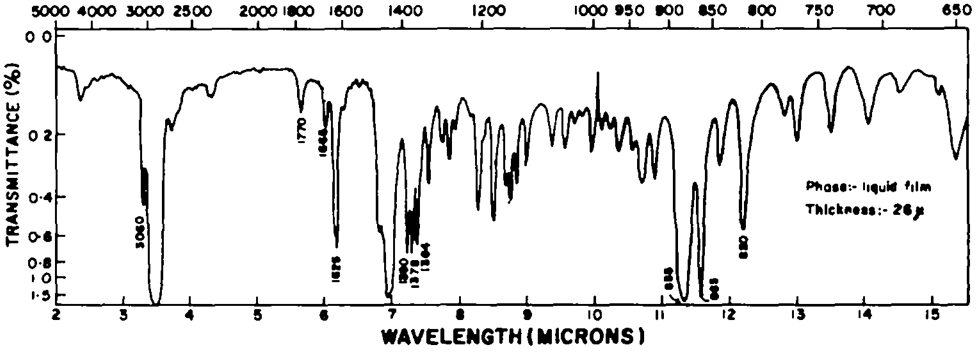

FIG. 2 Infra-red spectrum of α-himachalene

thus, himachalenes belong to a newer type. It is also clear from the above that α- and β-himachalenes differ from each other only in the position of an ethylenic linkage(s).

Structural features. In the IR spectrum (Fig. 2) α-himachalene displays bands assignable to $>C{=}CH_2$ (3060, 1770, 1625 and 885 cm^{-1}) and $>C{=}CH—$ (1665 and 865* cm^{-1}). These assignments are fully supported by its PMR spectrum (Fig. 4) and that of its dihydro derivative (readily obtainable by its hydrogenation in ethanolic solution). On the lower field strength side, α-himachalene shows a signal† (2H, almost a s) at 283 c/s and another at 322 c/s (1H, broad s) assignable[8] to protons on a vinylidene group and a trisubstituted ethylenic linkage respectively. In accordance with these assignments, dihydro-α-himachalene shows absorption only for $>C{=}CH—$ (IR: 1657, 862 cm^{-1}; PMR: 1H, broad s at 328 c/s).

β-Himachalene shows absorption due to one $>C{=}CH—$ linkage only: IR (Fig. 3) 1665, 857 cm^{-1}; PMR (Fig. 5): 1H, partly split signal centred at 319 c/s.

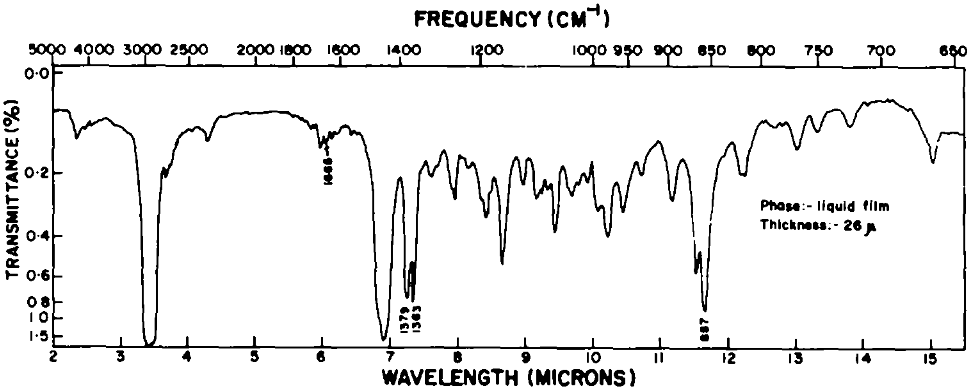

FIG. 3 Infra-red spectrum of β-himachalene

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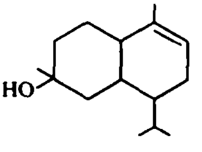
* Though the spectrum of α-himachalene shows a band at 820 cm^{-1}, which is well within the range for out-of-plane bending of a trisubstituted ethylenic linkage (800–840 cm^{-1})[6], it has not been assigned to this mode of vibration because, in β-himachalene which also contains the same linkage (*vide* subsequent discussion) this absorption is very much reduced while that at 858 cm^{-1} is quite strong. Moreover, dihydro-α-himachalene in which the vinylidene linkage has been reduced but, which still contains the trisubstituted olefinic bond, a peak is observed only at 862 cm^{-1}.

From the present work which unequivocally establishes the structures of himachalenes, it becomes clear that in these compounds the out-of-plane bending vibration of hydrogen on a trisubstituted double bond lies at abnormally higher frequencies. Another similar case is that of δ-cadinol(i)[7], where the bend occurs at 873 cm^{-1}.



Ii

† S = singlet; d = doublet; etc

In view of our previous data, then, the other olefinic linkage must be tetrasubstituted. However, in order to rule out the remote possibility of β-himachalene containing a cyclopropane ring,* rather than another olefinic linkage, the end absorption[10–12] in the UV of α-himachalene, dihydro-α-himachalene and β-himachalene have been measured (Table 2) and the data support the presence of a tetrasubstituted olefinic linkage in β-himachalene.

TABLE 2. END ABSORPTION

	ε210	ε215	ε220	ε225
α-Himachalene	8705	3635	950	630
β-Himachalene	7840	6950	4330	2870
Dihydro-α-himachalene	2320	1270	695	375
Trisubstituted olefinic bond[12]	1400–4700	600–3500	250–1800	—
Tetrasubstituted olefinic bond[12]	4400–10,000	3900–9200	3400–6700	—

The PMR spectrum of α-himachalene (Fig. 4) clearly reveals the presence of two quaternary Me's (sharp, partly overlapping 3H signals at 58, 60 c/s) and one Me on an olefinic linkage (3H signal at 108 c/s). These assignments are borne out from the spectrum of its dihydro-derivative (3H sharp signals at 55 and 59 c/s; 3H d centred at 55 c/s, $J = 6$ c/s, assignable to —CH—$C\underline{H}_3$; $C\underline{H}_3$—C=C signal at 100 c/s). β-Himachalene (Fig. 5) displays signals for two quaternary Me's (44 and 58 c/s signals) and two vinylic Me's (6H signal at 104 c/s).

Determination of the carbon skeleton. To gain insight into the carbon frame-work of himachalenes, the dehydrogenation of these hydrocarbons was investigated.

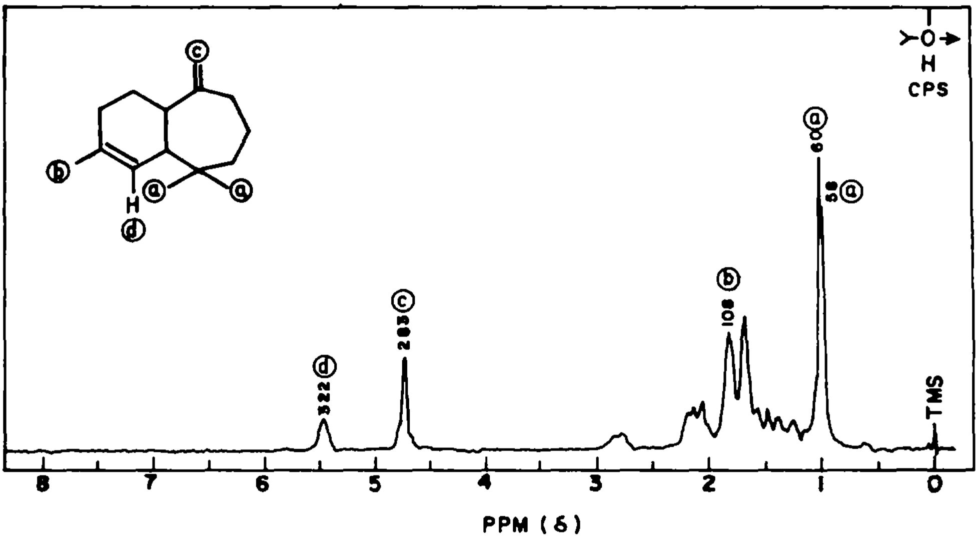


FIG. 4 PMR Spectrum of α-himachalene

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* This was thought desirable, especially, in view of the higher discrepancy of M_D of β-himachalene and, also keeping in mind that the formation of dihydrochloride and tetrahydroderivative could also arise from the rupture of a cyclopropane ring. Peracid titration has been found to be abnormal in some cases.[9]

Pure α-himachalene or pure β-himachalene on Se dehydrogenation yielded an identical reaction product (GLC). In view of this, large scale experiments were carried out on a mixture of these hydrocarbons (1 : 1) which was more easily available.

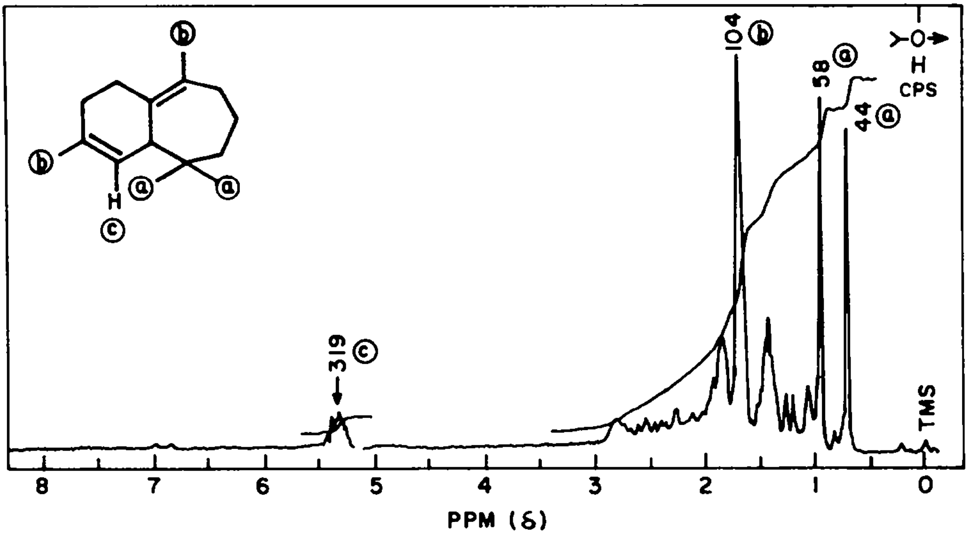
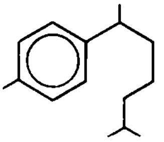
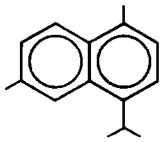


FIG. 5 PMR Spectrum of β-himachalene

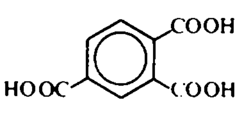
Himachalenes, on Se dehydrogenation (305–310°/48 hr) yielded three main products (A, B and C) in the ratio of 39(A), 28(B) and 30(C)%. However, on S-dehydrogenation (210–215°/2 hr) the product consisted essentially of A (56%) and B (33%), only traces of C (< 5%) being formed. Fractional distillation of Se dehydrogenation product yielded A and C more or less in a pure state. The first component A, was readily identified as 2-methyl-6-(*p*-tolyl)-heptane (I) by comparison (physical constants, UV and IR spectra) with an authentic sample; likewise component C was readily recognized as cadalene (II). For the characterization of compound B, sulphur dehydrogenation product was oxidized with HNO_3 yielding terephthalic acid and trimellitic acid (III); hence, compound B must be a 1,2,4-trisubstituted benzene. This was clearly borne out from a study of the IR absorption in the 1650–1950 cm^{-1} region.[6] A comparison of this pattern (Fig. 6) with those for I and 2-methyl benzosuberane (IV) (Fig. 6) clearly shows that the absorption pattern due to S-dehydrogenation product (mixture of A and B), is clearly a summation of patterns due to benzene substitution types represented by I and IV.



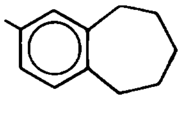
I



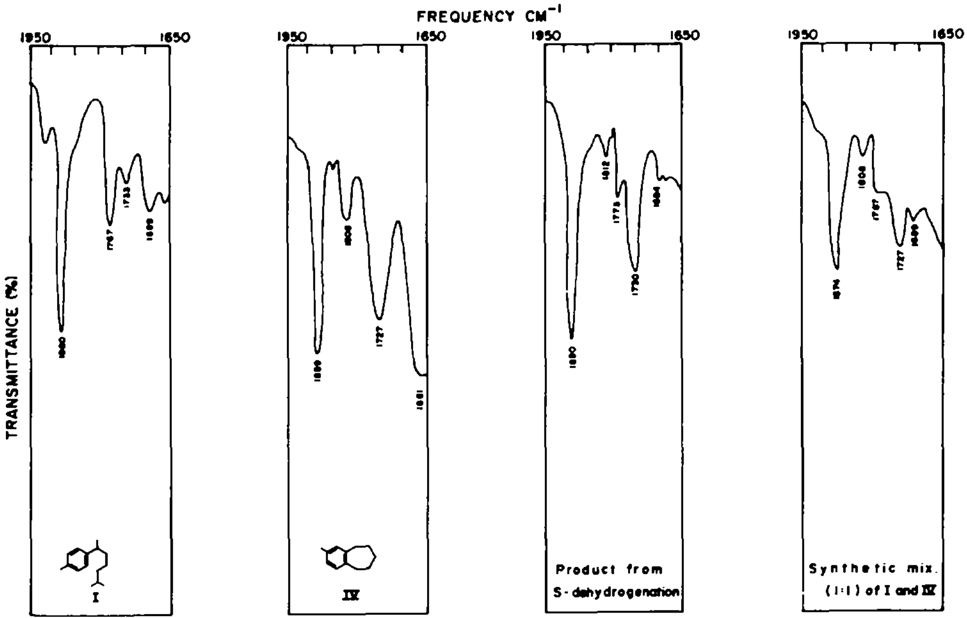
II



III



IV



(a) 1:4 DISUBSTITUTION (b) 1:2:4 TRISUBSTITUTION (c) (d)

FIG. 6 Aromatic substitution patterns (1959–1650 cm^{-1} region)

From the above data it is concluded that himachalenes have a carbon skeleton capable of scission to a species that can, later, give rise to both 2-methyl-(6-p-tolyl)-heptane (I) and cadalene (II)* and, component B, may as well represent the original carbon frame-work of himachalenes.

Taking into consideration the above experimental results it becomes apparent that himachalenes have a carbon-skeleton (V) with carbon 1 attached to a position on the other part of the molecule. Noting the fact that β-himachalene has one tetra-substituted ethylenic linkage and, further, bearing in mind the nature of the methyls, the linkage in V must be between C_1 and C_{11}; structure VI stands ruled out as it would have one terminus of the tetrasubstituted olefinic linkage at the bridge-head and this is sterically prohibitive.[18] Thus, the carbon frame-work of himachalenes

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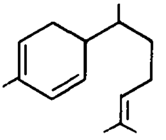
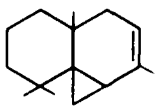
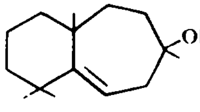
* Though the cyclization of a monocyclic sesquiterpene of type corresponding to I, namely zingiberene (ii), to cadalene during dehydrogenation is known, the reverse case, i.e. the formation of I from a bicyclic sesquiterpene of cadalene type, has not been reported so far[13–15] and appears unlikely.



ii

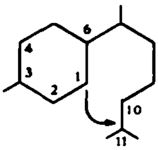


iii

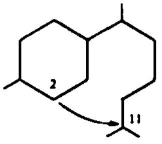


iv

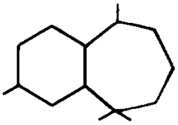
In connection with this it may be noted that thujopsene[16] (iii) and widdrol[17] (iv) on Se-dehydrogenation give 1,7-dimethyl-4-isopropylnaphthalene.



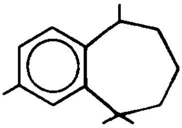
V



VI



VII



VIII

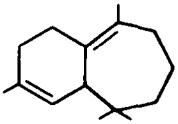
may be provisionally represented as VII whence, product B of dehydrogenation becomes VIII.[*]

In order to gain clear experimental support for the presence of a geminal dimethyl group in himachalenes and, thus adduce evidence in favour of C_1–C_{11} linkage, nitric acid oxidation of himachalenes was investigated. The acids produced on oxidation were converted into methyl esters and their composition established by GLC. The various components were isolated by a combination of fractionation and partition chromatography and characterized by comparison with authentic samples. In this way the products of oxidation were established as:

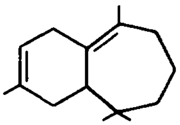
dimethylmalonic acid	4%
α,α-dimethylsuccinic acid	20%
α,α-dimethylglutaric acid	38%
α,α-dimethyladipic acid	13%
succinic acid	25%

These results clearly establish the carbon frame-work of himachalenes as VII.

Structure of β*-himachalene.* Based on the above considerations, β-himachalene may be represented by IX or X. Of these structures IX is preferred because of this



IX



X

isolation of significant amount of succinic acid during the HNO_3 oxidation. Unequivocal evidence supporting the structure IX for β-himachalene came from the results of oxidative ozonolysis. The acidic portion was esterified and its GLC showed the presence of at least three components in the ratio 36, 43 and 20%. These were separated by fractionation and preparative GLC. The lowest boiling component

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[*] This product has been obtained in a state of purity by a two-step sequence from β-himachalene and its structure confirmed by a total synthesis. These results are described in the following communication. The compound has been found to occur in the essential oil of Cedrus deodara (unpublished results of S.C. Bisarya) and has been named *ar*-himachalene.

(36 %) was readily identified as methyl levulinate. The next component (43 %) was also a keto-ester and was identified as methyl geronate (XI) by comparison of its semicarbazone with that from an authentic sample (prepared from β-ionone).[19] The highest

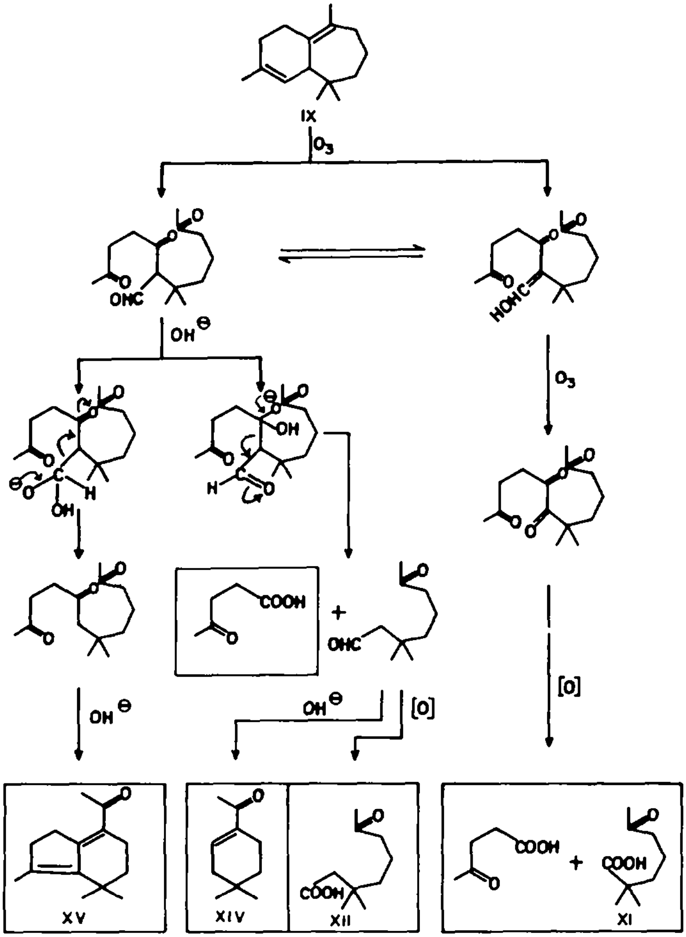
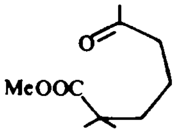


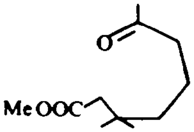
Fig. 7 Ozonolysis of β-himachalene

boiling component (20 %) was also a methyl ketone (+ve iodoform test; $\nu^{C=O}$ 1720 cm^{-1}). On mechanistic considerations (Fig. 7) this component was thought to be methyl homogeronate (XII) (methyl ε-acetyl-ββ-dimethyl-caproate), a conclusion which was confirmed by comparison with an authentic sample synthesized* from tetrahydroeucarvone (XIII).

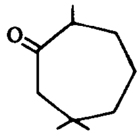
* ε-Acetyl-ββ-dimethylcaproic acid has been prepared by Baeyer and Villiger[20] by KMnO$_4$ oxidation of tetrahydroeucarvone. The following procedure proved to be far superior. Tetrahydroeucarvone was subjected to base-catalysed ethyl nitrite-ketone fission[21] and the intermediate oxamino ester directly converted into XII by treatment with formalin and hydrochloric acid.



XI



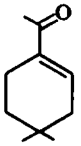
XII



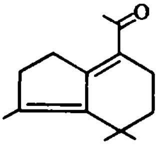
XIII

Since the neutral fraction was bound to contain polyketones and cyclized products, it was further treated with base to isolate identifiable products. Thus, after alkali treatment two pure products could be isolated. The lower boiling ketone was isolated as its semicarbazone (m.p. 215–217°; λ_{max} 257 mμ, ε 26,240) and was expected, on mechanistic considerations, to be 1-acetyl-4,4-dimethylcyclohexene (XIV).[22] This was confirmed by direct comparison with a sample synthesized* from 4,4-dimethyl-Δ^2-cyclohexenone.

The second unsaturated ketone was also isolated through its semicarbazone and it analysed for $C_{14}H_{20}O$. From its λ_{max} 317 mμ (ε 18,200) it is clearly an αβ, γδ-dienone.



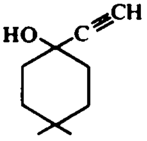
XIV



XV

In the IR spectrum (Fig. 8) it shows bands for C=O (1647 cm^{-1}) and C=C (1531 cm^{-1}).† The PMR spectrum (Fig. 9) shows the presence of two quaternary Me's (6H sharp s at 52 c/s), one olefinic Me and one C$\underline{H}_3$CO (6H s at 126 c/s) and no

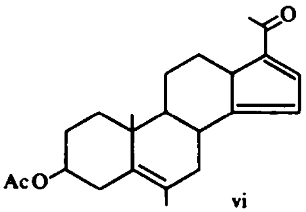
* The following route proved superior to the reported method.[22] Base-catalysed addition of methyl vinyl ketone to isobutyraldehyde gave 4,4-dimethyl-Δ^2-cyclohexenone[23] which was hydrogenated to the saturated ketone. Ethynylation of the latter, in presence of potassium t-amyloxide yielded v which rearranged to XIV in excellent yield by heating in aq. acetic acid with mercury treated resin.[24]



V

This preparation was kindly carried out by Mr. K. C. Srivastava.

† Though this value for $\nu^{C=O}$ would appear to be rather low, a similar case (vi; $\nu^{C=C}$ 1534 cm^{-1})[25] may be pointed out.



vi

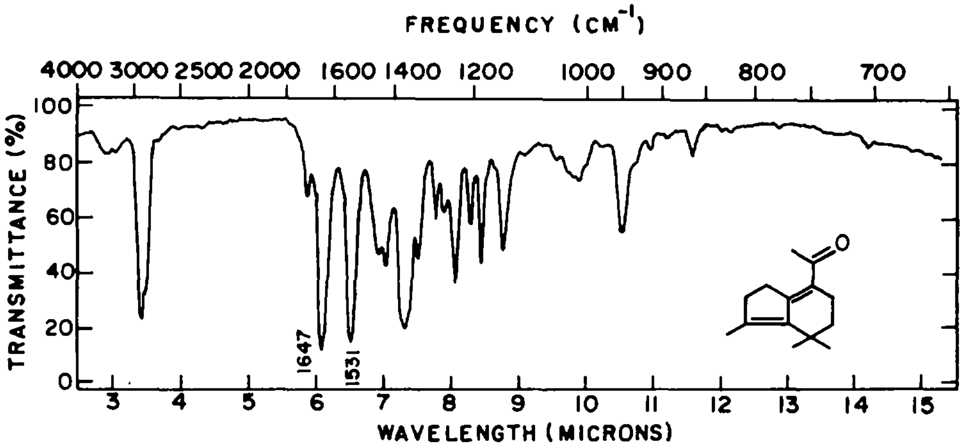


Fig. 8 IR Spectrum of dienone XV

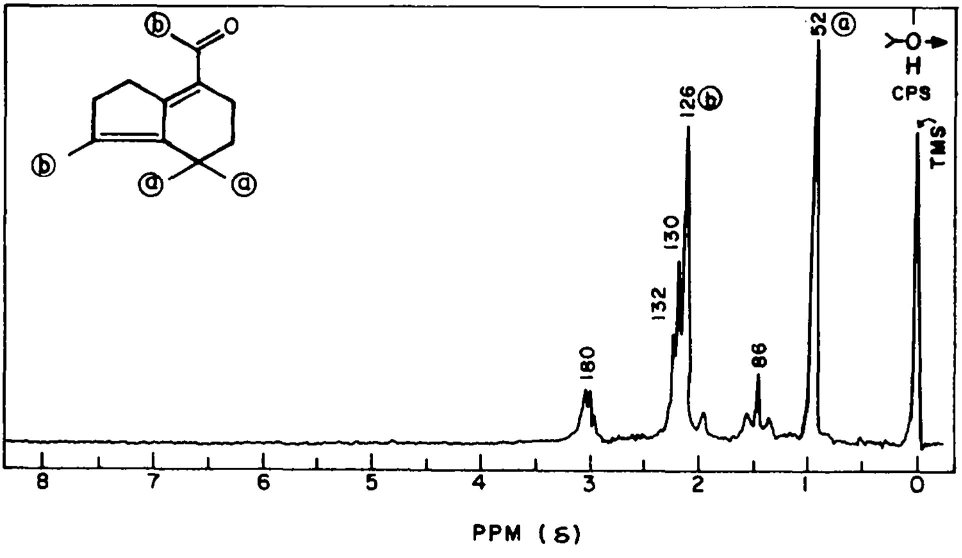
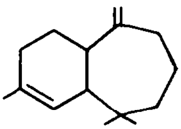


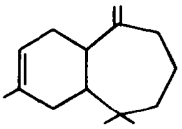
Fig. 9 PMR Spectrum of dienone XV

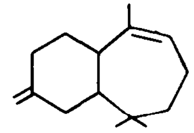
olefinic proton; the assignments to the signals centred at 86 and 180 c/s (each 2H) are indicated in the Fig. 9 (and are consistent with the PMR spectrum of XIV). These data are in full accord with the structure XV, expected on mechanistic reasoning.

The isolation and complete characterization of the above products, the genesis of which is readily rationalized on the basis of structure IX for β-himachalene (Fig. 7), fully confirm this structure.

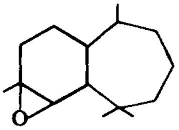
Structure of α-himachalene. On the basis of the carbon-skeleton established for himachalenes, and the structural features deduced for α-himachalene, three gross structures (XVI–XVIII) come for consideration for this hydrocarbon. Of these XVI is preferable on biogenetic considerations discussed later. Support for this formula for α-himachalene was gathered as follows. Dihydro-α-himachalene on epoxidation


XVI

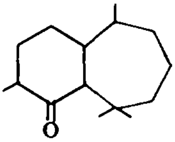

XVII


XVIII

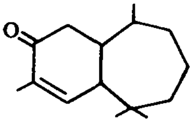
yielded an oxide (PMR spectrum: Me on carbon attached to oxygen, 3H s at 76 c/s; 1,2-epoxide ring proton, 1H signal at 165 c/s, essentially a s) which on brief treatment with $BF_3 \cdot Et_2O$ at −10° smoothly passed into a ketone ($\nu^{C=O}$ 1697 cm^{-1}), which in the IR does not show any absorption ~1410 cm^{-1} (scissoring frequency of a methylene group adjacent to $>C=O$).[6] The formation of such a ketone is possible only on the basis of structure XVI for α-himachalene and the epoxide and the ketone can now be represented as XIX and XX respectively.



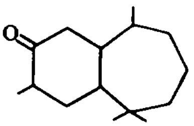
XIX



XX



XXI

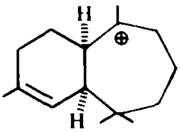


XXII

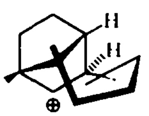
Further support for XVI was obtained by the sodium dichromate–acetic acid oxidation[26] of dihydro-α-himachalene when an αβ-unsaturated ketone (XXI) (λ_{max} 244 mμ, ε 15880; IR: C=O 1680 cm^{-1}; PMR: one vinyl proton signal at 339 c/s) was obtained, which on hydrogenation yielded the dihydroketone (XXII) (IR: C=O 1720 cm^{-1}) and this, as expected, showed a clear absorption peak at 1406 cm^{-1} in its IR spectrum.

The above results clearly define the gross structure of α-himachalene as XVI.

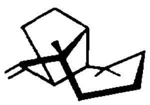
Biogenetic considerations. The structures of α- and β-himachalenes, deduced above, can, in principle, arise directly by proton-elimination from the species XXIII, first suggested[27] as the hypothetical precursor for the longibornyl cation (XXIV).[28] The



XXIII



XXIV


XXV

species XXIII should give rise to α-himachalene with *cis*-junction and, this has been established experimentally (Part XXXI of this series). Thus the biogenesis of himachalenes (and related compounds) and that of longifolene (XXV) and its congeners appears to be intimately linked.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Pet. ether refers to the fraction b.p. 40–60°. All solvent extracts were finally washed with brine, before drying (Na_2SO_4). Optical rotations were taken in $CHCl_3$. For tetranitromethane (TNM) tests, equal amounts of undiluted compound and 10% solution of the reagent in $CHCl_3$ were mixed.

UV spectra were taken on a Perkin–Elmer spectrophotometer, model 350, in 95% EtOH. IR spectra were taken on a Perkin–Elmer Infracord, model 137E as smears. All PMR spectra were taken in 10–20% soln in CCl_4 with TMS as an internal standard, on a Varian Associates A-60 spectrometer; peaks are reported in c/s from TMS.

GLC was carried out on a Perkin–Elmer Vapour Fractometer, model 154-D, using H_2 as the carrier gas and a 2-meter column (external diam 6 mm) packed with 20% diethylene glycol polysuccinate on Chromosorb W, unless stated to the contrary.

Isolation of himachalenes. The essential oil of *Cedrus deodara* (1760 g; supplied by the Regional Research Laboratory, Jammu, India) was carefully fractionated through a glass helices packed column,* carrying a total-condensation type still-head; a reflux ratio of 1:15 was maintained. The course of fractionation was followed by determining the $[\alpha]_D$ (neat) and GLC (130°, 15 lb psi) of each cut (40–50 ml). Cuts 3–9 (256 g, b.p. 105–107°/4 mm, $[\alpha]_D$ −71 to −40°) and cuts 16–32 (780 g, b.p. 120–125°/4 mm, $[\alpha]_D$ +120 to +200°) were pooled separately for the isolation of α- and β-himachalene respectively.

Refractionation of these two pools, separately, yielded 75 g of GLC pure α-himachalene (Found: C, 88·22; H, 11·77. $C_{15}H_{24}$ requires: C, 88·16; H, 11·84%) and 140 g of pure β-himachalene (Found: C, 88·20; H, 11·79. $C_{15}H_{24}$ requires: C, 88·16; H, 11·84%) respectively. Both the compounds are colourless liquids, with pronounced odour of the wood; their physical constants are given in Table 1.

Hydrochlorides

Himachalene dihydrochloride.[1] An ice-cooled soln of the hydrocarbon (2 g, α- or β-himachalene) in 4 ml of gl. AcOH was saturated with dry HCl and the deep coloured product left overnight at ca. −5°. The product was filtered off and recrystallized from benzene–pet. ether (1:4) to give long, white needles, m.p. 118–119° (with dec), yield 1·2 g. The $[\alpha]_D^{30}$ of the dihydrochloride (*c*, 10% in $CHCl_3$) was dependent on age of the solution: +5·6° (0·5 hr), +21·3° (1 hr), +28·2° (1·5 hr), +32·1° (2·5 hr) +32·0° (8 hr).

Himachalene monohydrochloride.[1] A soln of the dihydrochloride (0·7 g) in dry MeOH (4 ml), on keeping at 0° for 2 days, deposited white needles (0·4 g) which after two recrystallizations from MeOH furnished 0·2 g of a product m.p. 52–53°, $[\alpha]_D^{32}$ +123·0° (stable).

Peracid oxidations

To a known quantity of α-himachalene (0·4557 g) or β-himachalene (0·4595 g), an excess of percamphoric acid in $CHCl_3$ (0·2581N, 75 ml) was added (at 0°) and the reaction allowed to proceed at that temp and followed iodometrically in the usual manner. The reaction was found to be essentially complete after 2 hr, with very little change thereafter; at the end of 24 hr period, 1·96 and 1·93 mole equiv of the peracid had been consumed by α- and β-himachalene respectively. The reaction mixtures were filtered and the filtrates worked up by washing with 5% $NaHCO_3$ aq and drying.

Removal of solvent under reduced press at room temp gave *α-himachalene dioxide* as white flakes, m.p. 125–126° (pet. ether), $[\alpha]_D^{30}$ −144° (*c*, 0·25%). Found: C, 76·40; H, 10·40. $C_{15}H_{24}O_2$ requires: C, 76·22; H, 10·24%). β-*Himachalene dioxide* was obtained as a liquid: b.p. 126–130°/2 mm, n_D^{26} 1·4939, $[\alpha]_D^{26}$ +87° (*c*, 2·0%). (Found: C, 75·91; H, 10·12. $C_{15}H_{24}O_2$ requires: C, 76·22; H, 10·24%).

Tetrahydrohimachalenes

(i) *From α-himachalene.* α-Himachalene (0·4808 g) in gl. AcOH (50 ml) over pre-reduced Adam's Pt catalyst (50 mg) absorbed 140 ml (2·148 mole equiv) H_2 during 2 hr at 24°/693 mm, when further absorption of H_2 stopped. The reaction mixture was worked up in the usual manner to give the tetrahydroderivative as a colorless liquid: b.p. 132°/14 mm, n_D^{24} 1·4862, d_4^{24} 0·8986, M_D 66·48 (calc. 67·07), $[\alpha]_D^{24}$ −8·25° (*c*, 8·48%); TNM test, -ve. (Found: C, 86·57; H, 13·39. $C_{15}H_{28}$ requires; C, 86·46; H, 13·54%).

(ii) *From β-himachalene.* β-Himachalene (0·585 g) in gl. AcOH (40 ml) over pre-reduced Adam's Pt catalyst (85 mg) absorbed 167 ml (2·15 mole equiv) H_2 during 8 hr at 27°/708 mm. The product (TNM test,

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* Supplied by Emil Greiner and Co., New York; the estimated number of theoretical plates under the above working conditions is ca. 30.

–ve) was obtained as a colourless liquid: b.p. 110–111°/3 mm, $n_D^{26\cdot5}$ 1·4876, $d_4^{26\cdot5}$ 0·8997, M_D 66·65 (Calc. 67·07), $[\alpha]_D^{24}$ –21·05° (*c*, 4·28%). (Found: C, 86·58; H, 13·39. $C_{15}H_{28}$ requires: C, 86·46; H, 13·54%).

Dihydro-α-himachalene

α-Himachalene (0·384 g) in EtOH (50 ml) was hydrogenated over prereduced Adam's Pt catalyst (50 mg), when 50 ml (1 mole equiv) H_2 was absorbed during 1 hr at 22°/693 mm, after which further absorption ceased. The usual work-up gave dihydro-α-himachalene (0·33 g) as a colorless liquid: b.p. 98–100°/2 mm, n_D^{24} 1·4972, d_4^{24} 0·9105, M_D 66·24 (Calc. 66·63), $[\alpha]_D^{24}$ +59·17° (*c*, 3·4%). PMR spectrum: quaternary methyls 55, 59 c/s; —CH$\underline{\text{Me}}$ d centred at 56 c/s, J = 6 c/s; =C—$\underline{\text{Me}}$ 100 c/s, slightly broadened s; C=C$\underline{\text{H}}$ 328 c/s, broad s, half-band width 8 c/s. (Found: C, 87·40; H, 12·58. $C_{15}H_{26}$ requires: C, 87·30; H, 12·70%).

Dehydrogenations

(i) *Selenium dehydrogenation of pure himachalenes.* α-Himachalene (1 g) and Se (1·5 g) were mixed and heated first at 270–280° (15 hr) and finally at 320–325° (36 hr). The product (0·5 g) was isolated by distillation and then redistillation over Na: b.p. 100–108°/2 mm, n_D^{24} 1·5279; GLC (polyethylene glycol, 214°, 25 lb psi) showed three components A, B and C in the ratio 39:28:30. β-Himachalene (1 g) likewise, gave a product (0·55 g): b.p. 98–107°/2 mm, n_D^{22} 1·5340; A, B and C (GLC) in the ratio 42:31:24.

Selenium dehydrogenation of himachalenes mixture and isolation of products

On a preparative scale, the hydrocarbon mixture (9 g, 1:1 mixture) and Se (14 g) were heated together at 305–310° for 48 hr and worked up by direct distillation. The product (11·4 g) from two such experiments was roughly fractionated (6 in-Vigreux column):

Frac. 1 (3·16 g): b.p. 126–130°/10 mm, n_D^{24} 1·4911
Frac. 2 (1·42 g): b.p. 133–140°/10 mm, n_D^{24} 1·5038
Frac. 3 (1·30 g): b.p. 143–153°/10 mm, n_D^{24} 1·5353
Frac. 4 (1·88 g): b.p. 128°/2 mm, n_D^{24} 1·5720

Fractions 1 and 4 consisted essentially of compounds A and C respectively and were utilised for their identification.

2-Methyl-6-(p-*tolyl*)-*heptane* (I, *compound* A). Fraction 1 on passing through a column of Al_2O_3/I (basic) (19 cm × 2·5 cm) gave pure 2-methyl-6-(p-tolyl)-heptane (2·57 g) using pet. ether as eluent (25 ml × 4): b.p. 125–126°/11 mm, n_D^{26} 1·4887, d_4^{26} 0·8678, M_D 67·87 (Calc. 67·87); $\lambda_{max}^{heptane}$ 260, 265 and 273 mμ; IR spectrum was superimposable on that of an authentic sample (see below). (Found: C, 88·21; H, 11·77. $C_{15}H_{24}$ requires: C, 88·16; H, 11·84%).

Fraction 1 (97 mg) was added to HNO_3 aq. (1·2 ml conc HNO_3 and 2·5 ml H_2O) and heated in a sealed tube at 195 ± 5°/16 hr. The product was evaporated to dryness and made free from HNO_3 by repeated evaporations with water on a steam-bath. The residue (56 mg, m.p. > 340°) was esterified with diazomethane in ether to give a methyl ester, m.p. 138–140°, mixed m.p. with dimethyl terephthalate (m.p. 140°) was 139–140°.

An authentic sample of I was prepared by the dehydrogenation[29] of bisabolenes[30] (3·6 g) with selenium (5 g) at 260–280°/30 hr. Direct distillation gave a product (2·3 g) which was redistilled over Na and the distillate (1·8 g) purified further by shaking its soln in pet. ether (30 ml) with 95% H_2SO_4 (5 ml). The usual work up gave pure 2-methyl-6-(*p*-tolyl) heptane (1·4 g), as an oil: b.p. 133–136°/16 mm, n_D^{32} 1·4868; $\lambda_{max}^{heptane}$ 260 (ε, 402), 265 (ε, 505) and 273 mμ (ε, 545); IR spectrum (liquid): st. bands at 722, 818, 1020, 1110, 1168, 1512 cm^{-1}. (Found: C, 88·30; H, 12·00. $C_{15}H_{24}$ requires: C, 88·16; H, 11·84%).

Cadalene (II, *compound* C). Fraction 4 (1·88 g) was treated with trinitrobenzene (1 g) in alcohol (15 ml) and the product (1·5 g, yellow needles collected, m.p. 108–109°, mixed m.p. with an authentic sample of trinitrobenzene-cadalene complex (m.p. 112–113°) was 110–111°. The complex (1 g) was passed through a column of basic Al_2O_3/I (20 cm × 1 cm) using pet. ether as solvent and eluent to obtain the pure hydrocarbon (0·49 g): b.p. 118°/1·3 mm, n_D^{30} 1·5810; $\lambda_{max}^{heptane}$ 232 (ε, 59,160), 290 (ε, 6,310) and 325 mμ (ε, 699). (Lit.[31] b.p. 149°/10 mm, n_D^{19} 1·5851; λ_{max} 228, 232, 280, 284, 295, 310, 317 and 325 mμ; trinitrobenzene complex, m.p. 112–113°).

(iii) *Sulphur dehydrogenation of himachalenes mixture* (*for compound* B). A mixture of himachalenes (15 g) and S (7·5 g) was heated together at 210–215°/250 mm for 2 hr and directly distilled and the yellow distillate (7·5 g) redistilled over Na. The product was diluted with pet. ether (30 ml) and shaken with 95% H_2SO_4 (10 ml) for 1 hr to remove olefins. The organic layer was separated and worked up to yield a material

(3·6 g): b.p. 113–119°/6 mm, n_D^{21} 1·5044; Br_2 in CCl_4 not decolorized; its GLC showed A, B and C in the ratio 14:8:1.

The above product (0·195 g) was oxidized with HNO_3, as described earlier for I, and the product (0·179 g) was repeatedly leached with small volumes of water. The residue (49 mg, m.p. >340°) was identified as terephthalic acid, as described earlier.

The aq. washings from the above were taken to dryness and the resulting solid (110 mg, m.p. 180–190°) crystallized from benzene-acetone (2:1) when a product (55 mg), m.p. 202–208° was obtained, mixed m.p. with an authentic sample of trimellitic acid (m.p. 208–213°, prepared by HNO_3 oxidation of 2-methyl-*p*-cymene) was 203–212°. This acid on being heated at 250–260°/1 hr, followed by sublimation (0·6 mm) yielded the anhydride (35 mg), m.p. 153–157°, purified by resublimation, m.p. 160–162°, mixed m.p. with an authentic sample (m.p. 160–164°) was 160–163°. (Found: C, 55·61; H, 2·60. $C_9H_4O_5$ requires: C, 55·26; H, 2·10%).

Nitric acid oxidation

A mixture of HNO_3 (400 ml, $d^{25} = 1·31$) and vanadium pentoxide (0·4 g) was heated to 100° with stirring and the himachalenes mixture (~1:1; 13 g) introduced dropwise (20 min). After the evolution of oxides of N_2 had ceased (1·5 hr) the reaction mixture was refluxed (oil-bath, 145–150°) with stirring for 3 hr and then evaporated to dryness on a steam-bath. To the residue conc HNO_3 (30 ml) was added and again taken to dryness. The product was diluted with water and the soln evaporated and the process repeated till the product was free from HNO_3. The resulting material was taken up in MeOH (15 ml) and benzene (30 ml) and after adding H_2SO_4 (3 ml), refluxed for 13 hr. The benzene layer was separated, the aq layer diluted with water (150 ml) and extracted with ether (30 ml × 3). The combined organic layers were washed free of acid ($NaHCO_3$ aq) and dried; removal of solvent, followed by distillation gave a product (2·2 g), b.p. 87–102°/25 mm. The GLC (polyethylene glycol, 213°, 25 psi) of this material showed it to consist of 5 components, a, b, c, d and e (increasing retention time order) in the ratio, stated earlier.

The above experiment was repeated several times to collect a total of 16·2 g of this material, which was carefully fractionated on a spinning band column, with the results summarised in Table 3. Fractions 1, 4, 6 and 7 were employed for the characterization of the various components.

TABLE 3 FRACTIONATION OF HNO_3 OXIDATION PRODUCTS

Frac.	Wt. (g)	b.p./10 mm	n_D^{28}	GLC analysis
1	0·37	68°	1·4121	only a
2	1·29	74°	1·4160	a:b/40:60
3	2·41	78°	1·4190	b:c/50:50
4	3·30	87–89°	1·4210	b:c/40:60
5	3·88	96–101°	1·4241	b:c:d/12:24:64
6	3·24	107–109°	1·4260	d:e/82:18
7	0·96	113–116°	1·4280	d:e/27:73

Dimethylmalonic acid (comp a). Frac. 1 (83 mg) was heated on a waterbath for 15 hr with conc HCl (1 ml), gl. AcOH (0·6 ml) and water (0·4 ml) and the product taken to dryness to give a material (58 mg), m.p. 130–150°. This was recrystallized from benzene-MeOH (2:1) to give cubes, m.p. 186–187°, mixed m.p. with an authentic sample of dimethylmalonic acid (m.p. 191–193°) was 186–187° [Found: C, 45·20; H, 6·10; Neut. equiv. 67·7. $C_5H_8O_4$ requires: C, 45·45; H, 6·10%; Neut. equiv. 66·1].

Succinic acid, αα-dimethylsuccinic acid (compds b, c). Frac. 4 (0·5 g) was hydrolysed with HClaq, as above, and the crude acid (0·33 g, m.p. 116–145°) crystallized once from acetone-benzene (1:1, 6 ml) and then from water (1 ml) to give a pure acid (40 mg), m.p. 184·5–185·5°, identified as succinic acid by mixed m.p. with an authentic sample (m.p. 185·5–186·5°), when no depression was observed.

In another experiment the above crude acid mixture (85 mg) was separated by partition chromatography*

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* In all partition chromatography experiments, silica gel (BDH) was heated to 150–160°/20 hr before use. Chloroform refers to $CHCl_3$ saturated with water. The compound was dissolved in $CHCl_3$–n–BuOH (~1:1) and placed on the column which was then eluted with solvent mixtures.

on a column (20·5 × 2·2 cm) prepared from silica gel (35 g), chloroform (80 ml) and water (21 ml). The material was eluted with chloroform containing increasing amounts of n-butanol:

Frac. 1 0% n-BuOH 50 ml —
Frac. 2 5% n-BuOH 50 ml —
Frac. 3 10% n-BuOH 50 ml 6 mg m.p. 133–137°
Frac. 4 20% n-BuOH 50 ml 22 mg, m.p. 133–137°
Frac. 5 40% n-BuOH 50 ml 6 mg, m.p. 133–137°
Frac. 6 60% n-BuOH 50 ml 4 mg,
Frac. 7 80% n-BuOH 3 × 50 ml 18 mg, m.p. 172–179°

Frac. 3–5 were mixed and crystallized from benzene–acetone, to give a product, m.p. 139–140°, identified by mixed m.p. with an authentic sample (m.p. 140–141°) as αα-dimethylsuccinic acid. Frac. 7 was succinic acid (see above).

αα-Dimethylglutaric acid (*compd d*). Frac. 6 (0·5 g) was hydrolysed with HCl aq as above to obtain a product (0·41 g; m.p. 42–62°), which was purified by partition chromatography, following essentially the details given above. In this way from 98 mg of crude acid, 20% n-BuOH in $CHCl_3$ (4 × 16 ml) eluted 62 mg of an acid, m.p. 60–66°, repeatedly recrystallized from pet· ether to a product (20 mg), m.p. 81–82°. The product was identified as αα-dimethylglutaric acid by mixed m.p. with an authentic sample* (m.p. 81–82°).

αα-Dimethyladipic acid (*compd e*). Frac. 7 (0·6 g), on hydrolysis with HClaq gave a crude acid (0·52 g), m.p. 60–67°. A part of it (0·21 g) was chromatographed on a column (20 × 2·6 cm) prepared from silica gel (50 g), $CHCl_3$ (120 ml) and water (30 ml). A major fraction (88 mg, m.p. 73–76°) was eluted by $CHCl_3$ (2 × 50 ml) and was recrystallized from pet. ether–ether mixture to give an acid (40 mg), m.p. 87·5–89°, identified as αα-dimethyladipic acid by mixed m.p. with an authentic sample[32] (m.p. 88–89°). (Found: C, 54·90; H, 7·87. $C_8H_{14}O_4$ requires: C, 55·16; H, 8·10%).

The acid was further characterized by dry distilling 100 mg of the crude acid with iron powder (100 mg) and $Ba(OH)_2$ (20 mg). The distillate was directly converted into its *2,4-dinitrophenyl-hydrazone* (HCl method) which was recrystallized from EtOH, orange needles, m.p. 137–138°, mixed m.p. with an authentic sample[32] m.p. 141–142°) of the 2,4-dinitrophenylhydrazone of αα-dimethylcyclopentanone was 138–140°.

GLC of esters. Once the component acids had been identified, the position of their methyl esters on the GL Chromatogram was confirmed by the peak accentuation method using authentic samples. This provided further confirmation of their identity. The relative retention times (polyethyleneglycol, 213°, 25 psi), in terms of dimethylsuccinate, for the dimethyl esters of the components a, b, d and e were 0·5, 0·81, 1·41 and 1·97 respectively.

Ozonolysis of β-himachalene

Ozonolysis. A soln of β-himachalene (2·26 g) in $ChCl_3$ (60 ml) was ozonised at − 10° by bubbling ozonized O_2 ($\sim$ 160 mg/hr) till it was no longer absorbed (ca. 5·5 hr; KI-boric acid test soln). The solvent was removed at room temp under suction and the product carefully warmed with H_2O_2 (30%, 5 ml), water (20 ml) and Na_2CO_3 (1 g), first at 60° (1 hr) and finally at $\sim$100° (2 hr). The product was cooled and extracted with ether (20 ml × 4) and the ether extracts washed with Na_2CO_3aq (10%, 15 ml × 3), and dried. On solvent removal, a viscous product (1·16 g) was obtained as the neutral fraction.

The aq alkaline soln was acidified (H_3PO_4), saturated with ammonium sulphate and extracted continuously (60 hr) with ether. The ether extracts, after the usual work-up, gave an acidic part (1 g), which was esterified with diazomethane.

Acidic products

GLC (160°, 15 psi) of the ester mixture, described above, showed it to consist of essentially 3 components (a, b, c) in the ratio 36, 43 and 20% having relative retention times of 1, 3·48 and 6·21 respectively. The 3 components were separated by preparative GLC (2 meters × 1·3 cm column, 160°, 15 psi) either from the total mixture or after a preliminary fractionation.

Methyl levulinate (*compd a*). Component a (0·25 g) was converted into its *semicarbazone* (pyridine method) and the resulting crude derivative (0·27 g, m.p. 125–127°) repeatedly crystallized from MeOH to furnish white needles, m.p. 142–143°, mixed m.p. with an authentic sample of the semicarbazone of methyl levulinate (m.p. 142–143°) was undepressed.

Similarly, a portion (60 mg) of this fraction was converted into the *2,4-dinitrophenylhydrazone* (HCl method): yellow needles (MeOH), m.p. 140–141°, undepressed by admixture with an authentic sample of 2,4-dinitrophenylhydrazone of methyl levulinate (m.p. 140–141°).

* Kindly prepared by J. R. Prahlad by following the directions of Wilcox and Mesirov.[32]

The IR spectrum of the component a was superimposable on that of an authentic sample of methyl levulinate.

Methyl geronate (*XI, compd b*). GLC fraction (0·2 g) corresponding to component b was converted into its *semicarbazone* (0·15 g), m.p. 130–140°, which was recrystallized twice from aq MeOH to give microprisms, m.p. 156–157°, mixed m.p. with an authentic sample (see below) of the semicarbazone of methyl geronate (m.p. 158–159°) was 157–158°. (Found: C, 55·10; H, 8·82; N, 17·83. $C_{11}H_{21}O_3N_3$ requires: C, 54·30; H, 8·70; N, 17·27%). A better analysis could not be obtained even with the authentic sample).

Methyl homogeronate (XII, *compd c*). GLC fraction corresponding to component c was identified as methyl homogeronate by preparation of derivatives and their comparision with authentic samples (see below).

Semicarbazone, shining flakes (MeOH), m.p. 114–116°, mixed m.p. with an authentic sample (m.p. 115–116°) remained undepressed.

2,4-*Dinitrophenylhydrazone*, yellow needles (MeOH), m.p. 92–93°, mixed m.p. with an authentic sample (m.p. 92–93°) was same. (Found: C, 53·90; H, 6·30. $C_{17}H_{24}O_6N_4$ requires: C, 53·67; H, 6·36%).

Neutral products

The neutral portion (4 g from 3 experiments) was refluxed with KOH aq (5%, 400 ml) and EtOH (50 ml) for 3 hr (N_2). The product was worked up in the usual manner and the crude material fractionated to get two essentially pure fractions: (a), 0·3 g, b.p. 87–94°/4 mm, n_D^{29} 1·4909, λ_{max}^{EtOH} 232 mμ, ε 6000; (b), 0·95 g, b.p. 130–136°/2 mm n_D^{29} 1·5292, λ_{max}^{EtOH} 317 mμ, ε 6900.

1-*Acetyl-4,4-dimethylcyclohexene* (XIV). Fraction a was converted into its *semicarbazone* (pyridine method), which was recrystallized from EtOH to give white shining flakes, m.p. 216–217°, λ_{max}^{EtOH} 257 mμ (ε 26,240); mixed m.p. with an authentic sample of the semicarbazone of 1-acetyl-4,4-dimethylcyclohexene (see below) (m.p. 214–216°) was 215–216°. (Found: C, 62·90; H, 9·10; N, 19·90. $C_{11}H_{19}ON_3$ requires: C, 63·12; H, 9·15; N, 20·08%).

The above semicarbazone (30 mg) was warmed with 2,4-dinitrophenylhydrazine reagent (prepared from from 30 mg of reagent 5 ml of EtOH and a drop of conc H_2SO_4) for a few min and the new derivative (44 mg, m.p. 181–183°) collected after several hr. The 2,4-*dinitrophenylhydrazone* was recrystallized from EtOH to give glistening red needles, m.p. 183–184°, $\lambda_{max}^{CHCl_3}$ 254 (ε 16,740), 385 mμ (ε 27,550); mixed m.p. with an authentic sample of 2,4-dinitrophenylhydrazone of 1-acetyl-4,4-dimethylcyclohexene (m.p. 182–183°) was 182–183°. (Found: C, 58·30; H, 6·10. $C_{16}H_{20}O_4N_4$ requires: C, 57·82; H, 6·07%).

2-*Acetyl-5,5,7-trimethyl-bicyclo*[4.3.0] $\Delta^{1,6}$ nonadiene (XV). Fraction b was converted into its *semicarbazone* (pyridine method), which was recrystallized several times from EtOH and EtOH-benzene (1:9) to give a solid, m.p. 209–210° (Found: C, 68·90; H, 8·50; N, 15·70. $C_{15}H_{23}ON_3$ requires: C, 68·93; H, 8·67; N, 16·08%).

The above semicarbazone (0·15 g), oxalic acid (0·3 g), water (3 ml) and n-heptane (10 ml) were mixed and refluxed with stirring till a clear soln was obtained (0·5 hr). The reaction mixture was worked up in the usual manner to give the regenerated ketone, which was distilled: pale yellow oil (76 mg), b.p. 136°/2 mm (bath temp), n_D^{30} 1·5310. (Found: C, 82·90; H, 10·20. $C_{14}H_{20}O$ requires: C, 82·30; H, 9·87%).

The semicarbazone was converted into the corresponding 2,4-*dinitrophenylhydrazone*, as described for XIV, and was obtained as brown red micro-crystals, m.p. 188–189°. (Found: C, 62·26; H, 6·60. $C_{20}H_{24}O_4N_4$ requires: C, 62·48; H, 6·29%).

Dihydro-α-himachalene epoxide (XIX)

Dihydro-α-himachalene (6·9 g, 0·0335 mole) was mixed slowly with an excess of a $CHCl_3$ soln of perbenzoic acid (0·6304N, 120 ml i.e. 0·0378 mole) at 0°. After 72 hr, the product was washed free of acid (10% Na_2CO_3 aq) and dried. The solvent was removed and the product (6·879 g, 93%) distilled, b.p. 110–115°/2 mm, n_D^{30} 1·4881. An analytical sample was prepared by passing the epoxide (1·08 g) through a column of neutral alumina (grade II, 33 g, 16 × 1·6 cm) when a major portion (0·65 g) was eluted by pet. ether (50 ml × 8), b.p. 115–117°/2·5 mm, n_D^{30} 1·4873, $[\alpha]_D^{30}$ +20·61° (*c*, 7·51%); IR spectrum:  $\overset{O}{C—C}$ 880, 875, 810 cm^{-1}. (Found: C, 81·51; H, 11·92. $C_{15}H_{26}O$ requires: C, 81·02; H, 11·79%).

Isomerization of the epoxide (XIX) *to the ketone* (XX)

A soln of the above epoxide (6·88 g) in toluene (170 ml) was concentrated (oil-bath, 120–130°) to ~150 ml to remove traces of moisture. The soln was, next, cooled to −10° and freshly distilled BF_3–etherate (4·5 ml) slowly mixed. After 2 hr at − 10°, pyridine (10 ml) was added and the product washed with HClaq (~3N, 20 ml), brine and dried. The solvent was removed and the product distilled: b.p. 108–112°/2·5 mm, n_D^{30} 1·4920, yield 4·86 g. GLC of the product showed it to contain ~25% unchanged epoxide, besides the required ketone.

In an attempt to separate the above mixture, it (4·8 g) was subjected to column chromatography over Al_2O_3 (neutral/II, 23 cm × 3·1 cm), however the different fractions collected were shown to be mixtures* by GLC. Consequently, these fractions were mixed and the separation effected by preparative GLC (3 meters × 2·5 cm column, 200°, N_2, 15 psi). The required component was obtained as a solid, which crystallized from pet. ether in colourless prisms, m.p. 42–43°, $[\alpha]_D^{27}$ −93·56° (*c*, 3·42%). (Found: C, 80·80; H, 11·90. $C_{15}H_{26}O$ requires: C, 81·02; H, 11·79%).

The ketone failed to give a semicarbazone or a 2,4-dinitrophenylhydrazone by the usual methods.

Allylic oxidation of dihydro-α-himachalene

Dihydro-α-himachalene (0·95 g) was stirred with sodium dichromate (3 g) in gl. AcOH (45 ml) at 65–70° for 8 hr. EtOH (2 ml) was added to the reaction mixture, which was then diluted with water (30 ml) and extracted with benzene (20 ml × 5) and the extracts washed with Na_2CO_3aq and dried. The solvent was removed and the residue distilled: b.p. 118–121°/0·8 mm, n_D^{32} 1·5036, yield 0·75 g.

The above product was converted into its *semicarbazone* (pyridine method) which after recrystallization (EtOH) gave white needles, m.p. 208–209°, λ_{max}^{EtOH} 271 mμ (ε 34,570). (Found: N, 15·00. $C_{16}H_{27}ON_3$ requires: N, 15·15%).

Pure ketone was regenerated from its semicarbazone (1 g) by refluxing it with aq oxalic acid. After the usual work-up a solid (0·8 g) was obtained which was crystallized from pet. ether to give colourless prisms, m.p. 50–51°, $[\alpha]_D^{30}$ +93·04 (*c*, 4·17%), λ_{max}^{EtOH} 244 mμ (ε 15,880). PMR spectrum: two quaternary Me's 64, 71 c/s; CH_2–CH, 3H d, centred at 63 c/s, $J = 6$ c/s; vinyl Me, somewhat broad s centred at 94 c/s; vinyl proton, 1H broad s at 339 c/s. (Found: C, 81·75; H, 10·90. $C_{15}H_{24}O$ requires: C, 81·76; H, 10·98%).

2,4-*Dinitrophenylhydrazone* (from the semicarbazone by H_2SO_4 method) bright red needles (EtOH), m.p. 155–156°, λ_{max}^{EtOH} 257 (ε 20,120), 386 mμ (ε 32,880). (Found: N, 14·00. $C_{21}H_{28}O_4N_4$ requires: N, 13·99%).

Hydrogenation of unsaturated ketone XXI

The unsaturated ketone (0·486 g) in EtOH (30 ml) over pre. reduced Pd on $CaCO_3$ (1·25%, 0·75 g) absorbed 80·8 ml (1·36 mole equiv) H_2 at 23°/685 mm during 6 hr. The product was worked up in the usual manner and distilled to give a colorless liquid (0·48 g), b.p. 116°/1·2 mm. An analytical sample of the saturated ketone was prepared via its semicarbazone (described below) by oxalic acid treatment: b.p. 114°/1 mm, n_D^{26} 1·4970, d_4^{24} 0·9828, M_D 66·13 (calc. 67·09), $[\alpha]_D$ +52·2° (*c*, 1·53%); $\lambda_{max}^{heptane}$ 289 mμ (ε 23·9). (Found: C, 81·12; H, 11·73. $C_{15}H_{26}O$ requires: C, 81·02; H, 11·79%).

The hydrogenation product (0·48 g) was converted into its *semicarbazone* (pyridine method) which after recrystallization (EtOH) gave a white powder, m.p. 185–186°. (Found: N, 15·17; $C_{16}H_{29}ON_3$ requires: N, 15·04%).

A part of the saturated ketone (80 mg) was converted into 2,4-*dinitrophenylhydrazone* which was crystallized (EtOH) thrice to give yellow micro needles, m.p. 130–132°, λ_{max}^{EtOH} 362 mμ (ε 23,130). (Found: N, 14·13. $C_{21}H_{30}O_4N_4$ requires: N, 13·92%).

Methyl geronate (XI) *from β-ionone*[19]

Oxidative ozonolysis of β-ionone (4·69 g) in $CHCl_3$ (60 ml, containing 1% pyridine) was carried out as described earlier for β-himachalene and the acidic portion (~1 g) obtained was esterified (diazomethane). The product was fractionated and the fraction of b.p. 110–120°/10 mm (0·482 g), n_D^{30} 1·4490 was collected separately. This was converted into the semi-carbazone (pyridine method). Repeated recrystallization (MeOH) gave an authentic sample of the semicarbazone of methyl geronate, m.p. 158–159°. (Found: C, 54·94; H, 9·10; N, 17·97. $C_{11}H_{21}O_3N_3$ requires: C, 54·30; H, 8·70; N, 17·27%).

Methyl homogeronate (XII) *from tetrahydroeucarvone*

To a cooled soln (−10°) of MeONa in MeOH (from 0·3 g Na in 30 ml MeOH), tetrahydroeucarvone (1·855 g) was added, followed by ethyl nitrite (2 ml) and stirred for 1 hr. The product was kept at 0–2° for 24 hr. Through the yellow soln CO_2 was bubbled till no more ppt of Na_2CO_3 appeared (3 hr) when it

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* The mixture now contained (GLC) another component, besides the original two. Apparently epimerization of the ketone took place on the alumina column. This is further discussed in Part XXXI of this Series.

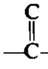
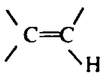
was filtered off. The filtrate was concentrated and treated with formaldehyde (40%, 2 ml) and 2N HCl (0·6 ml) and warmed on a water bath with swirling. The reaction mixture was cooled, diluted with water (50 ml) and extracted with ether (25 ml × 4); the ether extract was washed neutral with $NaHCO_3$ aq and dried. Solvent was removed and the residue distilled: the higher boiling fraction (1·397 g, 62% yield), b.p. 116–118°/3·5 mm, n_D^{30} 1·4370 was the required methyl homogeronate and was shown to be 97% pure by GLC. (Found: C, 65·60; H, 10·33. $C_{11}H_{20}O_3$ requires: C, 65·97; H, 10·07%).

The *semicarbazone* (pyridine method) was recrystallized from MeOH, m.p. 115–116°. The *2,4-dinitrophenylhydrazone* (H_2SO_4 method) after two recrystallizations from MeOH gave yellow needles, m.p. 92–93°. (Found: C, 54·08; H, 6·50. $C_{17}H_{24}O_6N_4$ requires: C, 53·67; H, 6·36%).

Synthesis of 1-acetyl-4,4-dimethylcyclohexene (XIV) (by K. C. Srivastava) *4,4-Dimethylcyclohexanone.* 4,4-Dimethylcyclohexene-2-one (2 g), as obtained by a known method,[23] was hydrogenated in EtOH (20 ml) over prereduced Pd–$CaCO_3$ (2%, 2 g); absorption of 1 mole equiv H_2 was over after 3 hr, when further absorption ceased. The usual work-up gave the required ketone (1·85 g), m.p. 38–40° (Lit.,[33] m.p. 38–40°). IR spectrum: C=O 1712 cm^{-1}. *Semicarbazone*, m.p. 196–198° (Lit.[33] m.p. 202°).

4,4-Dimethyl-1-ethynylcyclohexanol (V). To a saturated soln of acetylene[34] in ether (150 ml) at −15°, a soln of the above ketone (2 g) in ether (30 ml) and, a soln of KOA$^t_{m}$ (from 2 g K and 30 ml t-amyl alcohol) were introduced simultaneously, with stirring and under the usual precautions, during 2 hr. Acetylene was kept bubbling during the addition and for another 5 hr at a reduced rate. The reaction mixture was worked up with NH_4Cl in the usual manner and the crude product directly used in the next step.

1-*Acetyl-4,4-dimethylcyclohexene* (XIV). The above product was taken up in AcOH (12 ml) and water (1 ml) and after adding Hg-treated resin[24] (2 g) was heated under reflux for 1 hr. The catalyst was filtered off on cooling, the filtrate diluted with water (50 ml) and made slightly alkaline by 40% NaOHaq. The organic product was extracted with ether (50 ml × 3), dried and the solvent removed and the residue distilled to give the required compound as a colorless liquid, b.p. 80–83/8 mm, yield 1·8 g; λ_{max}^{EtOH} 232 (ε 11,400), 303 mμ (ε 46·5). IR spectrum: C=O 1656 cm^{-1}; C=C 1631 cm^{-1}. PMR Spectrum: two quaternary Me's,

6H s at 58 c/s;  $\overset{\overset{C}{\|}}{—C}—C\underline{H}_3$, 3H s at 134 c/s;  , 1H m centred at 409 c/s.

2,4-Dinitrophenylhydrazone, red needles (EtOH), m.p. 182–183° (Lit.[22] m.p. 185–186°). *Semicarbazone*, white flakes (EtOH), m.p. 214–216° (Lit.[22] m.p. 216–218°).

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