

ESSENTIAL OIL FROM *PREMNA TOMENTOSA*

BY V. LAKSHMI NARAYAN AND M. S. MUTHANA

(Department of Organic Chemistry, Indian Institute of Science, Bangalore-3)

ABSTRACT

Essential oil from *Premna tomentosa* obtained in 0.073% yield has been shown to contain limonene (57.8%), β -caryophyllene (17.2%), a new sesquiterpene hydrocarbon (7.8%), an unidentified sesquiterpene tertiary alcohol (5.6%) and an unidentified diterpene hydrocarbon (5.5%).

*Premna tomentosa*¹ is a tree often growing upto 50 feet, with fibrous bark, shredding off longitudinally in flakes. The tree belongs to Verbinacea species and is distributed widely in the Deccan, South Travancore and Ceylon, in deciduous forests upto an altitude of about 4,000 feet. The branchlets are covered with a dense yellow wool of stellate hairs. The leaves are 10 to 15 cm. long, ovate, rounded or subordinate at base. The flowers are on very short pubescent pedicles. An aromatic oil obtained from the roots is used locally as a remedy for stomach disorders. The wood from the tree is used in Mysore villages to make combs and similar articles used for toilet purposes.

Steam-Distillation of the Oil from the Leaves of Premna tomentosa

About 1,500 lb. of the green leaves were steam-distilled and about 500 gm. of the oil collected. The leaves were collected during the month of July and the yield of the oil on the average was 0.073 per cent., Table I.

TABLE I

Date of charging	Weight of leaves in lb.	Weight of oil in gm.	Percentage yield
10-7-1951	210	70	0.073
12-7-1951	266	90	0.074
14-7-1951	215	75	0.075
23-7-1951	203	65	0.071
25-7-1951	310	100	0.071
27-7-1951	300	100	0.073
Total	1,504	500	0.073

The oil obtained by steam-distillation had a fairly pleasant smell and a burning taste. It was light yellow in colour which gradually deepened in intensity on exposure to light.

TABLE II

1. Density	$d_{4}^{31.6^{\circ}}$	0.8740
2. Refraction Index	$n_{29^{\circ}}^D$	1.4862
3. Optical Rotation	$[\alpha]_{26^{\circ}C}^D$ in $CHCl_3$	+31.44°
4. Acid Number	Nil	
5. Ester Number		8.9
6. Acetyl Value		14.9
7. Unsaturation or Iodine Number		75.1

Fractionation of the Oil under Reduced Pressure.—The essential oil (320 g.) upon fractionation in a Towers distillation column furnished six fractions. As Fraction I has been obtained in small yield, its complete characterization has not been possible. Fraction II which constitutes about 57 per cent. of the essential oil consisted purely of a hydrocarbon which has been identified as a mixture of *d*- and *dl*-limonene. The hydrocarbon yielded nitrosochloride, m.p. 104°–05° C.; nitrol-benzylamine, m.p. 110° C.; dihydrochloride, m.p. 49–50° C. and tetrabromide, m.p. 124–25° C.: Fraction III which forms about 17 per cent. of the essential oil consisted chiefly of β -caryophyllene as indicated by its physical properties and easy formation of the blue nitrosite, m.p. 110° C. It further yielded the characteristic derivatives of β -caryophyllene; nitrosochloride, m.p. 160° C.; nitrolbenzylamine, 172° C.; β -caryophyllene alcohol, m.p. 95–96° C.

Fraction IV which forms about 7.8 per cent. of the essential oil appeared to be a new sesquiterpene hydrocarbon which formed a nitrosochloride, m.p. 152° C., and a nitrosate, m.p. 156–57° C. The melting points of these derivatives do not correspond to any known derivatives of sesquiterpene hydrocarbons.

After careful distillation over sodium, the hydrocarbon showed the following physical properties:

B.P.	70° C./0.1 mm.
$[\alpha]_{27^{\circ}}^D$	+ 18.13°

n_D^{27}	1.4995
$D_{26^\circ C.}^{26^\circ C.}$	0.9042
Molar Refractivity			..	66.30

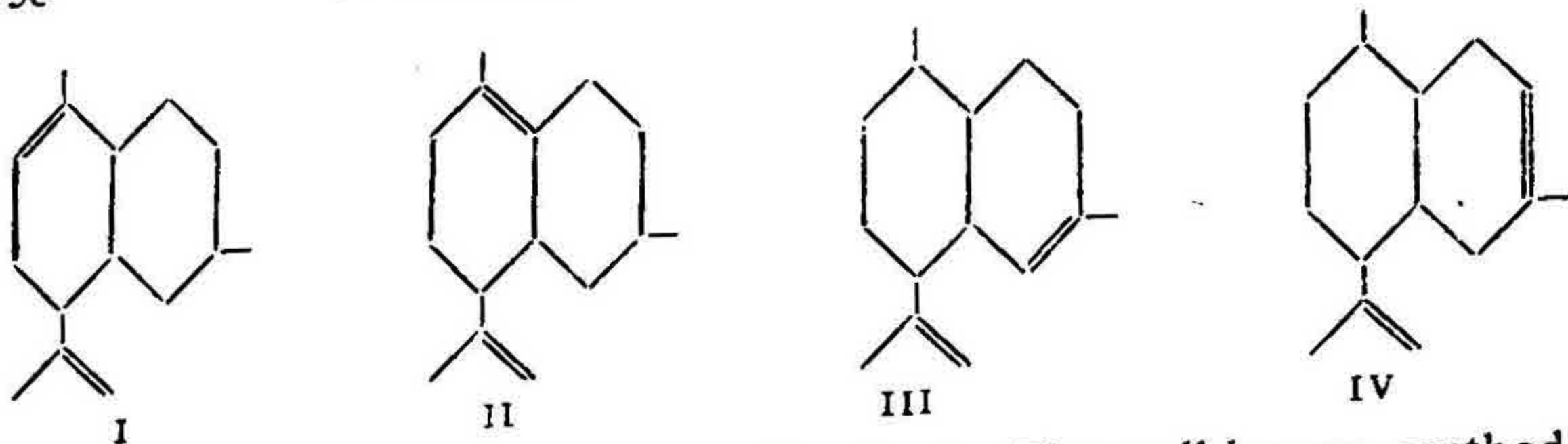
The molar refractivity agrees well with the value for a bicyclic sesquiterpene. Dehydrogenation with sulphur yielded cadalene which was identified through its picrate, m.p. $114^\circ C$. This indicated that the sesquiterpene is of the cadalene type. Ozonolysis of the hydrocarbon yielded a neutral product possessing a methyl keto group, formaldehyde and formic acid. As such, the presence of an exocyclic double bond in the hydrocarbon is indicated. Acetone could not be detected among the products of ozonolysis.

By adopting the procedure of Kolthoff and Lee² titration of the hydrocarbon with perbenzoic acid indicated the presence of one endocyclic and one exocyclic double bond. The negative response to Fieser's test³ for conjugated double bonds showed that the double bonds are probably non-conjugated.

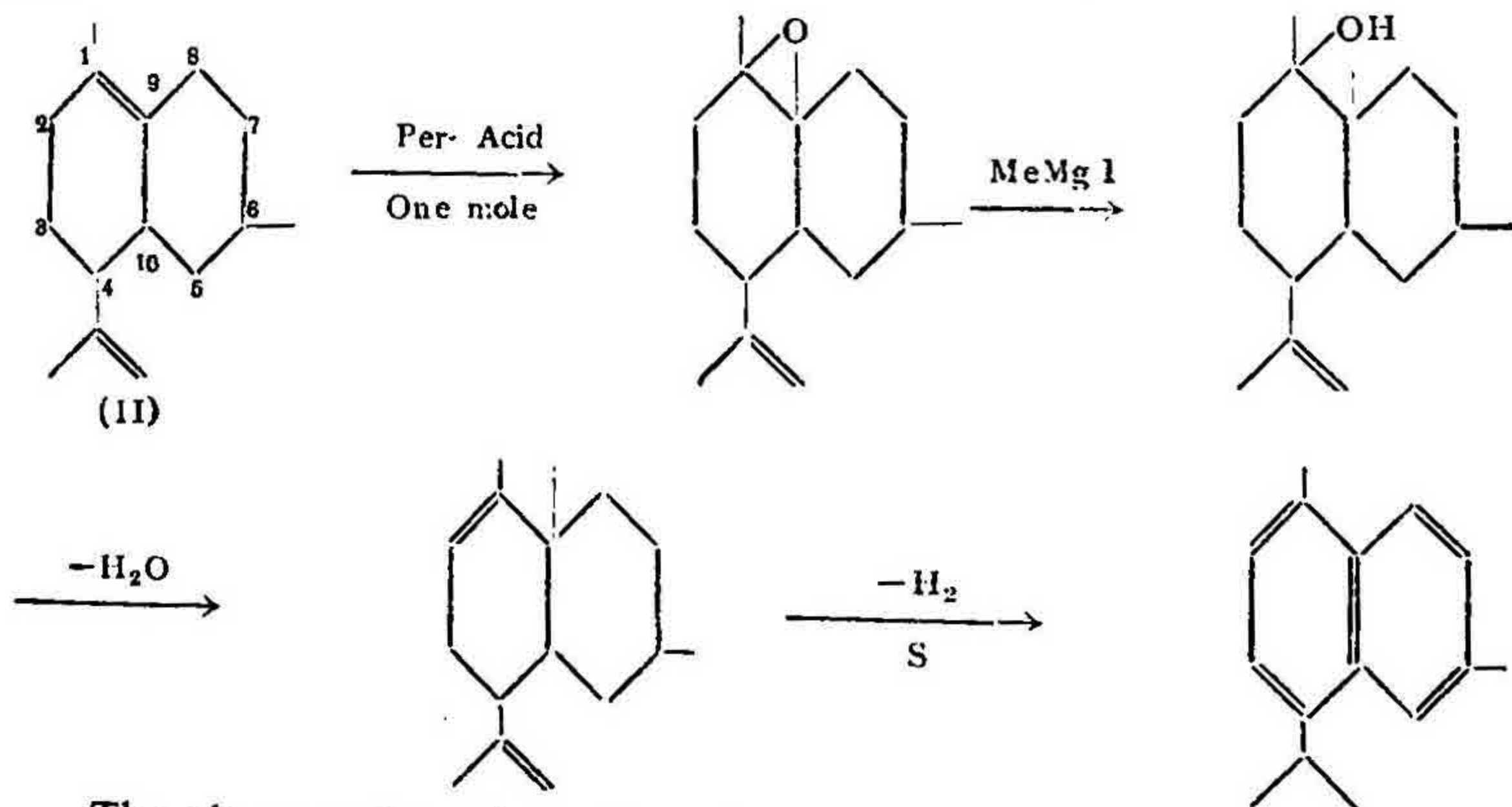
Position of the Exocyclic Double Bond.—One mole of the bicyclic sesquiterpene hydrocarbon was treated with one mole of perbenzoic acid, when the endocyclic double bond is first attacked and the epoxide formed. The epoxide was ozonized when the exocyclic double bond was eliminated as formaldehyde and formic acid. The ozonide obtained was decomposed by hydrogenation⁴ with gaseous hydrogen in the presence of palladium on barium sulphate as catalyst when a keto alcohol was obtained having molecular formula $C_{14}H_{24}O_2$, $D_{27^\circ C.}^{27^\circ C.}$ 1.042; n_D^{27} 1.5065 and molar refraction 63.97. The molar refraction calculated for a bicyclic keto alcohol comes to 63.99.

Estimation of methyl keto group by the haloform reaction gave a value of 0.87. This indicated the presence of one methyl keto group and that the exocyclic double bond is in the isopropyl side chain. Dehydrogenation of the keto alcohol with sulphur yielded a hydrocarbon which formed a picrate, m.p. $114^\circ C.$, and which showed a depression in m.p. by $14^\circ C.$ when admixed with cadalene picrate, m.p. $114^\circ C.$ The identity of this hydrocarbon remains to be established.

Estimation of methyl keto groups or potential methyl keto groups by chromic acid oxidation⁵ gave a value of 2. The above series of reactions reduces the possible positions occupied by the endocyclic double bond to the following four:



Position of the Endocyclic Double Bond.—The well-known method of Ruzicka and Sternbach⁶ of labelling the double bond with a methyl group by treating the epoxide with Grignard reagent was followed. The epoxide obtained by reacting the sesquiterpene hydrocarbon with molecular proportion of perbenzoic acid was treated with methyl magnesium iodide. The Grignard addition compound was decomposed with dilute hydrochloric acid and the crude product was dehydrated with 95 per cent. formic acid. The dehydrated product was dehydrogenated with sulphur, when only cadalene was isolated, characterized through its picrate, m.p. 114° C. No methyl cadalene could be isolated from the dehydrogenated product. This indicated that the endocyclic double bond might be attached to an angular carbon atom. The reactions carried out could be represented as below:



The above series of reactions indicate that the nuclear double bond may be in position 1-9. This is in agreement with the value of 2 obtained for methyl keto groups, estimated by chromic acid oxidation method, as also the absence of any aldehyde in the neutral product from ozonolysis. Therefore the new sesquiterpene hydrocarbon may be represented by the Structure II which fulfils the requirements of the reaction carried out and products obtained from the new sesquiterpene hydrocarbon.

Fraction V has been identified as a sesquiterpene tertiary alcohol, b.p. 180–82° C./0.1 mm. n_D^{27} 1.4985; $D_{27^\circ\text{C.}}^{27}$ 0.9432 and $[\alpha]_{27}^D + 11.2^\circ$ (Found: C = 81.90; H = 11.1, $\text{C}_{15}\text{H}_{24}\text{O}$ requires C = 81.82, H = 10.91%). Dehydrogenation by Melville's method^{6a} yielded cadalene identified through its picrate, m.p. 114° C. It does neither give positive xanthate reaction⁷ for primary and secondary alcohols, nor react with phthalic anhydride. Estimation of number of double bonds indicated the presence of two double bonds one of which was endocyclic and the other exocyclic. Further work regarding its constitution could not be carried out due to limited quantity of the compound.

Fraction VI, b.p. 180–82° C./0.5 mm., $n_D^{27} = 1.4795$, $D_{27}^{27} = 0.9030$, molar refractivity = 85.5 showed the presence of an exocyclic double bond by perbenzoic acid titration and ozonolysis when formaldehyde and formic acid were isolated. It did not yield any crystalline derivative. Dehydrogenation with sulphur did not give any picrate-forming aromatic hydrocarbon. Its molar refraction of 85.5 is in close agreement with the value 85.3 for a diterpene hydrocarbon containing one double bond. Further work could not be carried out due to limited amount of compound available.

EXPERIMENTAL

Essential Oil.—Green leaves (1,500 lb.) were steam-distilled in batches in a still with a capacity of about 300 lb. of leaves, at a steam pressure of about 30 lb./sq. in. The physical properties and chemical constants were determined according to standard procedures⁸ after drying the oil over anhydrous sodium sulphate. The constants are given in Table II.

Fractionation.—A batch of essential oil (320 gm.) was carefully fractionated through a glass helices-packed column of the total condensation variable take-off type (J. W. Towers & Co., Ltd.). Six fractions were collected with an approximate reflux ratio of 1:10. The properties of the various fractions are recorded in Table III.

TABLE III

No.	B.P.	$[\alpha]_{27}^D$	n_D^{27}	Ester No.	Iodine No.	D_{26}^{26}	Yield in gm.	Percentage yield
I	65–70° C./25 mm.	+33.5°	1.4475	138.50	53.9	0.8543	13	4.0
II	78° C./23 mm.	+66.34°	1.4750	11.80	36.34	0.8363	185	57.8
III	82–90° C./7 mm. ..	– 8.35°	1.4965	8.70	52.64	0.8960	55	17.2
IV	70° C./0.1 mm.	+17.86	1.5028	5.30	81.71	0.9042	25	7.8
V	180–200° C./1 mm. ..	+11.94	1.4985	21.12	60.50	0.9132	18	5.6
VI	180–200° C./0.5 mm.	+ 6.803	1.4795	14.6	36.6	0.9030	17	5.5

Identification of *d*- and *dl*-limonene from Fraction II

Molecular refraction for Fraction II turned out to be 0.53 units higher than the value 45.24 for a monocyclic terpene of formula $C_{10}H_{16}$. It was carefully refractionated in the Towar's column and five cuts were made as recorded in Table IV.

TABLE IV

No.	B.P.		n_{26}^D	$[\alpha]_{26}^D$	Weight in gm.
1	72-78° C./24 mm.	..	1.4600	+68°·24	12
2	80° C./24 mm.	1.4725	+75°·23	57
3	80° C. 24/mm.	1.4710	+79°·75	48
4	80° C./24 mm.	1.4730	+64°·23	40
5	80° C./24 mm.	1.4725	+65°·28	20

Crystalline derivatives like nitrosochloride, nitrol benzylamine dihydrochloride and tetrabromide were prepared according to standard methods.⁹ Mixed melting points of these derivatives with the corresponding ones from genuine sample of *d*-limonene remained undepressed. The results are summarised in Table V.

TABLE V

No.	Properties	<i>d</i> -limonene	Fraction II
1	B.P. ..	b_{760} 177.6-177.8° C. ¹⁰	b_{24} 80° C.
2	Density ..	$d_4^{20.6}$ 0.8117 ¹⁰	d_{26}^{26} 0.8363
3	Specific Rotation ..	$[\alpha]_D^{20}$ +126.8 ¹¹	$[\alpha]_D^{27}$ +66.34
4	Refraction Index ..	$n_D^{20.5}$ 1.473 ¹⁰	n_D^{27} 1.4750
5	Dihydrochloride ..	m.p. (<i>dl</i>) 49.50° C. ¹²	m.p. 49-50° C.
6	Tetrabromide ..	m.p. (<i>dl</i>) 125-26° C. ¹³	m.p. 124-25° C.
7	Nitrosochloride ..	m.p. 104 C. ¹⁴⁻¹⁶	m.p. 104-05° C.
8	Nitrolbenzylamine ..	m.p. 110° C. ^{14,16}	m.p. 110° C.

The low value of specific rotation, viz., $+66.34$ as compared to the value of $+126.8$ for pure *d*-limonene points out the fraction to be a mixture of *d*-limonene with an isomeric terpene. The nearly quantitative yield of dihydrochloride and that the bromide contains four atoms of bromine per mole of hydrocarbon restricts the possibilities to two, viz., *d*-limonene and terpinolene. But terpinolene tetrabromide has a m.p. of 117°C . and also no trace of acetone could be detected from among the products of ozonolysis. Hence the mixture can only be one of *d*- and *dl*-limonene.

Limonene tetrabromide.—To hydrocarbon (1 c.c.) diluted with ether (4 c.c.), cooled below 0°C ., bromine (0.7 c.c.) was added dropwise and the tetrabromide isolated after repeated crystallizations from a mixture of ethyl alcohol and ethyl acetate showed a m.p. $124-25^{\circ}\text{C}$.

Analysis.—Found: Br = 69.93; $\text{C}_{10}\text{H}_{16}\text{Br}_4$ requires Br = 70.17 per cent.

Ozonolysis of Hydrocarbon.—To hydrocarbon (5 c.c.) dissolved in pure and dry chloroform (100 c.c.) cooled below 0°C . was passed a rapid current of ozonized air. The issuing gases were bubbled through water (30 c.c.) in a trap cooled in ice. Formaldehyde was detected by preparing formal-dimethone derivative which was obtained as fine shiny needles, m.p. 188°C . Mixed m.p. with a genuine sample remained undepressed. Acetone was absent in the absorption trap.

Fraction III Identification of β -caryophyllene

Fraction III was carefully refractionated through a 8" column packed with glass helices and the following cuts were collected as in Table VI.

TABLE VI
Weight of Fraction 55 gm.

No.	B.P.	Specific rotation	Weight in gm.
1	$78-80^{\circ}\text{C}/12\text{ mm.}$	$+5^{\circ}.6$	2.0
2	$80^{\circ}\text{C}/7\text{ mm.}$	$-6^{\circ}.8$	2.0
3	$85^{\circ}\text{C}/7\text{ mm.}$	$-8^{\circ}.36$	10.0
4	$85^{\circ}\text{C}/7\text{ mm.}$	$-8^{\circ}.26$	20.0
5	$85^{\circ}\text{C}/7\text{ mm.}$	$-8^{\circ}.16$	15.0
6	$90^{\circ}\text{C}/7\text{ mm.}$	$-5^{\circ}.13$	4.0

The blue nitrosite, nitroso-chloride, nitrol-benzylamine and β -caryophyllene alcohol of β -caryophyllene were prepared according to standard methods.¹⁷

The properties are compared with those derived from β -caryophyllene in Table VII.

TABLE VII

No.	Properties	β -caryophyllene	Fraction III
1	B.P.	103–103.5° C./14 mm. ¹⁸	85°/7 mm.
2	Density	$d_4^{20^\circ\text{C}}$ 0.9075 ^{14,18}	D_{26}^0 0.8960
3	Refractive Index ..	n_D^{20} 1.4995 ^{14,18}	n_D^{27} 1.4965
4	Specific Rotation ..	$[\alpha]^D$ $-8^\circ.16$ ^{14,18}	$[\alpha]_D^{27}$ $-8^\circ.25$
5	M.P. of blue nitrosite ..	115° C. 110° C. ^{19,20}	110° C.
6	M.P. of nitrosochloride ..	159° C. ¹⁹	160° C.
7	M.P. of nitrolbenzylamine ..	172° C. ^{21,17}	172° C.
8	M.P. of β -caryophyllene alcohol	94–96° C. ¹⁷	95–96° C.

Mixed m.p.'s taken with corresponding derivatives from a genuine sample of β -caryophyllene remained undepressed.

Fraction IV: A New Sesquiterpene Hydrocarbon

Nitrosochloride.—Prepared according to standard method.⁹ The nitrosochloride recrystallized from benzene, m.p. 152° C. Analysis: Found: N = 5.15; $C_{15}H_{24}NOCl$ requires N = 5.2 per cent.

Nitrosate.—Prepared according to standard method.⁹ The nitrosate was recrystallized from benzene and was obtained in fine shining white plates, m.p. 156–57° C. Analysis: Found: N = 10.20; $C_{15}H_{24}N_2O_3$ requires N = 10.10 per cent.

Cadalene picrate

Dehydrogenation.—The hydrocarbon (1.0 g.) was dehydrogenated by heating with sulphur (0.48 g.) for 5 hours between 190–210° C. in a metal bath and the reaction product worked up in the usual manner and purified by distilling over sodium when liquid (0.4 g.) distilling between 130–35/5 mm. was collected. The liquid dissolved in 25 c.c. of petrol-ether was chromatographed through activated alumina (60-mesh) column 15 cm. \times 1 cm., and

collected in 5 c.c. lots. The residue obtained after removing solvent from second, third and fourth lots amounted to 0.35 gm. It formed the picrate easily which after repeated crystallizations showed constant m.p. of 114° C. Mixed m.p. with an authentic sample of cadalene picrate remained undepressed.

Ozonolysis.—To the terpene hydrocarbon (2 g.) dissolved in anhydrous acetone-free chloroform (150 c.c.) chilled in ice-salt freezing mixture, a rapid current of dry ozonised air was sucked in. The issuing gases were led through water (30 c.c.) cooled with ice. Ozonization was continued till no more ozone was absorbed by the solution (6 hours). Formaldehyde was detected in the issuing gases by the preparation of the characteristic dimedone derivative. M.p. 188, mixed m.p. with authentic sample undepressed.

Decomposition of the Ozonide.—The solvent was removed under vacuum at 30–40° C. with a thin current of dry air being sucked through the solution. The ozonide was obtained as a clear light yellow coloured syrup. It was heated under reflux with water (15 c.c.) very gradually, the apparatus being connected to a gas absorption trap containing water. The water in the gas absorption trap gave test for formaldehyde but did not give the test for acetone (Legal's test).

Separation of the Decomposition Products of Ozonolysis.—The reaction mixture containing the products of decomposition of the ozonide was extracted repeatedly with ether. The ethereal extract was washed with small quantity of water and added to the main aqueous solution (A). The ether extract was repeatedly extracted with dilute sodium carbonate solution to separate out the acidic constituents (B). The ether layer contained neutral constituents (C).

The aqueous portion (A) was acidic in character and indicated presence of formic acid by the mercuric oxide test.⁵

A portion of the aqueous solution gave formaldimethone, m.p. 188° C. Another portion treated with alkaline hydrogen peroxide solution (3 per cent.) and after standing for 24 hours distilled. The distillate did not give any test for acetone.

Acidic product (B) contained in sodium carbonate solution extract gave negligible amount of some gummy product on acidification. The neutral product in ethereal solution, on drying over anhydrous sodium sulphate and removal of ether furnished a thick reddish liquid (2 g.) which did not reduce either Tollen's Reagent or Fehling's solution, thereby showing the absence of any aldehyde. It gave positive iodoform reaction in dioxan solution and

showed positive reaction with 2:4-dinitrophenyl hydrazine for the presence of carbonyl group in the compound; but no derivative could be prepared.

Estimation of the Number of Double Bonds

To the terpene hydrocarbon (0.126 g.) in chloroform (5 c.c.) was added 0.2 N perbenzoic in chloroform (10 c.c.) and the solution cooled to zero. Excess of perbenzoic acid in aliquots were titrated iodimetrically from time to time and percentage of double bond attacked calculated. The data is given in Table VIII.

TABLE VIII

Time in hours	Thiosulphate equivalent to excess of perbenzoic acid	Percentage double bond attacked
0.5	0.9	40
1.0	1.25	56
2.0	1.48	65
4.0	1.68	75
8.0	1.80	80

A graph drawn with percentage of double bonds attacked against time and extrapolating the flat portion of the curve against the vertical axis, gave the percentage of the exocyclic double bonds, which was 50 per cent.

Determination of the Position of the Exocyclic Double Bond

Preparation of Mono-Oxide.—To a well cooled solution of the terpene (5 g.) in chloroform (80 c.c.) was added perbenzoic acid (3.6 g.) in chloroform (100 c.c.) similarly cooled. The reaction mixture was kept under ice-cold temperature for 1½ hours after which the solution was extracted thrice with 100 c.c. portions of an aqueous solution of sodium thiosulphate and sodium carbonate (300 c.c. water, 18 gm. sodium thiosulphate and 9 gm. of sodium carbonate). It was finally washed with water and dried over anhydrous sodium sulphate.

After removal of solvent, the epoxide was fractionated when liquid boiling 120–22/2 mm. $D_{26}^{26} = 0.9684$, $n_{26}^{D_{26}} = 1.5025$, $[\alpha]_{26}^D = -36.3$ was obtained in 3.5 gm. yield. Found: C = 80.67, H = 10.35, $C_{15}H_{24}O$ requires C = 81.8, H = 10.9 per cent.

Ozonolysis of the Mono-Oxide

The epoxide (3 g.) dissolved in glacial acetic acid was ozonised according to the procedure mentioned earlier; and the ozonide after removal of major portion of solvent was reduced catalytically by hydrogen in the presence of palladium catalyst on barium sulphate in a pressure bottle. About 400 c.c. of hydrogen was consumed at room temperature. The catalyst was filtered and acetic acid solvent removed under vacuum. The residual liquid was fractionated when a liquid boiling at $130^{\circ}\text{C./2 mm.}$ $D_{27^{\circ}\text{C.}}^{27^{\circ}\text{C.}} = 1.042$, $n_{27^{\circ}\text{C.}}^{\text{D}} = 1.5065$, was obtained in 2 gm. yield. The molecular refraction was calculated to be 63.94 while that for a bicyclic keto alcohol comes to 63.98. Found: C = 75.01, H = 10.8 per cent. $\text{C}_{14}\text{H}_{24}\text{O}_2$ requires C = 75.00, H = 10.71 per cent.

Estimation of Methyl Keto Group by the Iodoform Reaction

The keto alcohol (50 mgm.) dissolved in absolute methyl alcohol (free from acetone) was mixed with 0.1 N sodium hydroxide solution (20 c.c.); 0.0333 N iodine solution (75 c.c.) was added slowly during half an hour and allowed to stand for half an hour at 25°C. The solution was acidified with dilute hydrochloric acid and the excess iodine titrated against standard sodium thiosulphate solution. A blank estimation was simultaneously carried out. The number of methyl keto group was found to be equal to 0.87.

Estimation of the Terminal Methyl Number

The keto alcohol (47.4 mgm.) in a capsule was placed in a flask with 5 c.c. cold oxidizing mixture (from 20 c.c. concentrated sulphuric acid and 16.8 gm. of chromic anhydride diluted to 100 c.c. with water). The solution was heated under reflux with a micro-burner for $1\frac{1}{2}$ hours. The condenser was washed free of adhering acid, with water into the flask. Magnesium sulphate (7 gm.) was added and the solution steam-distilled. The distillate was titrated against 0.05 N barium hydroxide. The terminal methyl number is the number of mole equivalents of acetic acid produced from one mole equivalent of the compound. A blank experiment was simultaneously run. The terminal methyl number was found to be equal to 1.97.

Dehydrogenation of the Keto Alcohol

The keto alcohol (1 gm.) was dehydrogenated with sulphur (0.48 gm.) by the usual procedure mentioned earlier. After chromatographic separation of the products of dehydrogenation, a colourless liquid (0.1 gm.) was obtained which gave an orange yellow picrate which after recrystallization,

melted at 114° C. Mixed melting point with cadalene picrate (m.p. 114° C.) showed a depression in melting point by 14° C.

Determination of the Position of the Nuclear Double Bond

Preparation of the Mono-Oxide.—It was prepared as described earlier from the hydrocarbon (12 gm.) and the epoxide, b.p. 120–22/2 mm. (6 gm.) collected.

Reaction of the Monoxide with Grignard Reagent

Grignard Reagent was prepared from magnesium (2.6 gm.), methyl iodide (9.2 c.c.) and anhydrous ether (100 c.c.).

The Grignard solution was cooled in a freezing mixture and the monoxide (6 gm.) added slowly under constant shaking. After addition was complete, the mixture was kept for 15 minutes at ice temperature and then allowed to reach room temperature and then warmed under reflux for 48 hours. It was then decomposed with ice and dilute hydrochloric acid and ether layer separated and aqueous portion repeatedly extracted with ether. The combined ethereal extract was washed successively with a saturated solution of ammonium chloride, sodium-bisulphite and brine water containing sodium carbonate. The solution was then dried over anhydrous sodium sulphate. After removal of solvent, crude product (5.9 gm.) was dehydrated by heating on water-bath with 95 per cent. formic acid (15 c.c.) for 3 hours. The reaction product was worked out in the usual manner and a dark coloured liquid was obtained.

Dehydrogenation of the Dehydrated Grignard Product

The crude product (2 gm.) was dehydrogenated with sulphur (0.94 gm.) for 3 hours at 190–210° C. in the usual manner. The cooled product was extracted with benzene, treated with small quantity of norite, filtered and refluxed over sodium for 1 hour. After removal of solvent, the product fractionated. The highest boiling fraction (120–22°/5 mm., 0.5 gm.) gave the characteristic orange yellow picrate which after repeated crystallizations melted at 114° C. Mixed melting point with an authentic sample of cadalene picrate did not show any depression in m.p.

REFERENCES

1. Kirtikar and Basu
 2. Kolthoff and Lee
 3. Fieser
 4. Triebs, W.
- .. *Indian Medicinal Plants*, 1933, 3, 1929.
.. *J. Polymer Sci.*, 1947, 2, 206.
.. *J. Amer. Chem. Soc.*, 1938, 60, 168.
.. *Ber.*, 1947, 70, 62.

5. Pregl .. *Quantitative Organic Micro-Analysis*, III Edn., 1937, p. 201.
 Bartlet, W. B., *et al.* .. *Ind. Eng. Chem., Anal. Edn.*, 1944, 16, 434.
 Clark .. *Ibid.*, 1936, 8, 487.
6. Ruzicka and Sternback .. *Helv. Chim. Acta.*, 1940, 23, 124.
 6a Melville .. *J. Amer. Chem. Soc.*, 1933, 55, 2462.
7. Feigl .. *Qualitative Analysis by Spot Test*, 1947 Edn., p. 324.
8. Guenther .. *Essential Oils*, 1948, 1.
 9. _____ .. *Ibid.*, 1948, 2.
10. Richter, F. and Wolfe, W. .. *Ber.*, 1930, 63, 1724.
11. Braun, J. and Lenike, G. .. *Ibid.*, 1923, 56, 1563.
12. Hell, C. and Ritter, A. .. *Ibid.*, 1884, 17, 1978, 2610.
13. Wallach, O. .. *Ann.*, 1885, 227, 278.
 14. _____ .. *Ibid.*, 1892, 263, 264.
 15. _____ .. *Terpene and Camphor*, Leipzig, 1914, 271-82.
 16. _____ .. *Ibid.*
17. Sukh Dev and Guha, P. C. .. *J. Ind. Chem. Soc.*, 1949, 26, 319.
 .. *Ibid.*, 1948, 25, 495 ;
 Asahina and Tsukamoto .. *J. Pharm. Soc., Japan*, 1922, No. 484, 467-73.
18. Naves and Perrattet .. *Helv. Chim. Acta.*, 1941, 24, 796.
19. Deussen and Lewisohn .. *Ann.*, 1892, 359, 245.
 20. _____ .. *Ibid.*, 1907, 356, 13.
 Sukh Dev and Guha, P. C. .. *J. Ind. Chem. Soc.*, 1949, 26, 7.
21. Deussen and Lewisohn .. *Ann.*, 1908, 359, 245.
 _____ .. *Ibid.*, 1907, 356, 8.