
CHAPTER II

ISOLATION OF HIMACHALENES

The Tree

Cedrus deodara (Roxb) Loud, or Himalayan Cedar is a horizontal branched tree, growing to a height of 200 ft. with a girth of about 30 ft. in the Himalayan regions (4000 - 10,000 ft. high). The bark is brown with a whitish lustre. The leaves are long acicular in shape, grown on the branches in tufts 20 to 60 in numbers. Male catkins are more or less cylindrical and stamens are sub-cylindrical bilocular. Female cones are velvety and pea-green in colour and deliciously fragrant when young and become brown later. Seeds are unequal and somewhat wedge-shaped¹. The tree is known as Deodara in Sanskrit, Deodar in Hindi and Devataram in Malayalam. The tree yields valuable timber which is extensively used in making railway sleepers and door frames. During the process, a lot of waste wood is produced which in view of its high oil content is usefully employed for obtaining the oil by distillation².

THE ESSENTIAL OIL

Past work:

In 1916, Roberts³ made a preliminary study of the oil. He examined two samples of the oil which had the constants recorded in Table I. On fractionation of the oil, four main fractions were collected, one of which was identified as p-methyl- Δ^3 -tetrahydro acetophenone as its semicarbazone. The presence of a phenol was proved but its identity was not established due to its presence in low percentage. The main constituent (50 - 70%) of the oil was shown to be a sesquiterpene

TABLE I

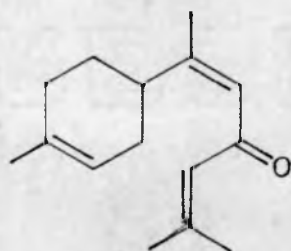
The Essential Oil : Physico-chemical data

Properties	Rao and Sukh Dev ⁷	Roberts ³	I.S.I. Standard*
Colour	Pale yellow	Reddish brown	Light yellow to reddish brown.
Odour	Characteristic odour of the wood.	Balsamic	Heavy balsamic.
Density	d_{31}^{31} 0.9277	d_{15}^{15} 0.9549, 0.9756	0.9323 to 0.9573
Optical rotation	$[\alpha]_D^{30}$ + 76.66°	$[\alpha]_D^{22}$ + 52.16° + 34.6	+20 to 62°
Refractive index	n_D^{31} 1.5095	n_D^{21} 1.5195, 1.5225	n_D^{30} 1.5038 to 1.5120
Acid value	0.065	5.6, 4.5	5
Ester value	3.85	19.3, 4.9	10 to 25
Acetyl value	5.6	30.8, 34.4	25 to 45

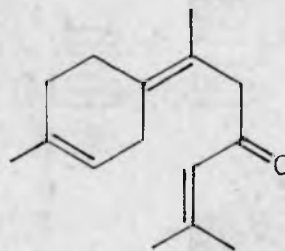
* Specifications for the oil of Himalayan Cedar wood I.S. 1615 - 1960.

fraction, for which he could not prepare a solid derivative. He could, however, isolate from the oil, hexoic, heptoic and stearic acids by hydrolysis.

In 1922, Simonsen and Rau⁴ confirmed the main work of Roberts. They did not find any phenol in the oil, but reported the presence of a viscid yellow sesquiterpene alcohol and some esters of fatty acids. In 1934, Pfau and Plattner⁵ examined a sample of the essential oil from the wood of the Himalayan Deodar and found that the higher boiling fraction of the oil also contained two isomeric ketones, namely α - and β -atlantones (1 and 2 respectively).



(1)



(2)

In 1944, Ruzicka and co-workers⁶ isolated a hydrocarbon fraction from the leaf oil of Cedrus atlantica, which formed an optically active crystalline dihydrochloride and monohydrochloride.

Work of Krishna Rao and Sukh Dev:

In 1952, Krishna Rao and Sukh Dev⁷ examined the oil more systematically.

They obtained the Deodar wood from Kangra in East Punjab and on steam distillation of the chipped wood, obtained the volatile oil in a yield of 10 - 11%. The oil was coloured yellow

and had the characteristic odour of the wood.

On careful fractionation of the oil through a packed column, five major fractions were collected. The first fraction contained a small percentage of alkali soluble portion (0.022%; benzoate, m.p. 74 - 75°C, copper salt, m.p. 132°C) but its identity was not proved due to lack of sufficient quantity of material. The bulk of fractions I and II was identified as a mixture of p-methyl acetophenone and p-methyl tetrahydro- Δ^3 -acetophenone. The presence of p-methyl tetrahydro- Δ^3 -acetophenone was confirmed by the oxidative regeneration of acetophenone from its semicarbazone by treatment with sulphuric acid (75%). The major portion of the oil (Fractions III and IV) was shown to consist of sesquiterpenes, named by these authors as α -himachalene (levo-rotatory) and β -himachalene (dextro-rotatory). Both these hydrocarbons yielded the same crystalline dihydrochloride with same melting point as that of Ruzicka's compound⁶. Himachalene dihydrochloride could be readily converted into a monohydrochloride having a melting point same as that reported by Ruzicka. However himachalene derivatives were found to be optically inactive. The last fraction was shown to consist essentially of a tertiary alcohol, termed, himachalol; traces of the atlantones were also identified in this fraction. The relationship of himachalol to the himachalenes was established by the preparation of the same dihydrochloride.

HIMACHALENES

Preliminary investigation by Krishna Rao and Sukh Dev on himachalenes had indicated that these hydrocarbons represent a new type in sesquiterpenes and the present work was undertaken to throw further light on the problem.

The essential oil obtained earlier by Krishna Rao and Sukh Dev was available for further investigation. On careful fractionation under reduced pressure, the oil yielded 15% of α -himachalene, ^{and} 45% of β -himachalene. The essential oil was cut into 35 fractions, the optical rotation and boiling point of each fraction being determined and those having identical properties being mixed up. A typical fractionation data is given in Table II (graphically represented in Fig.I).

In order to further purify these hydrocarbons, the respective α - and β - himachalene fractions (vide experimental) were again subjected to precise refractionation at a high reflux ratio, the optical rotation of each fraction being determined to gauge the course of the fractionation. The cuts with almost identical properties were mixed up.

The purity of these hydrocarbons was further checked by gas-liquid chromatography (GLC) and found to give a single peak under a variety of experimental conditions.

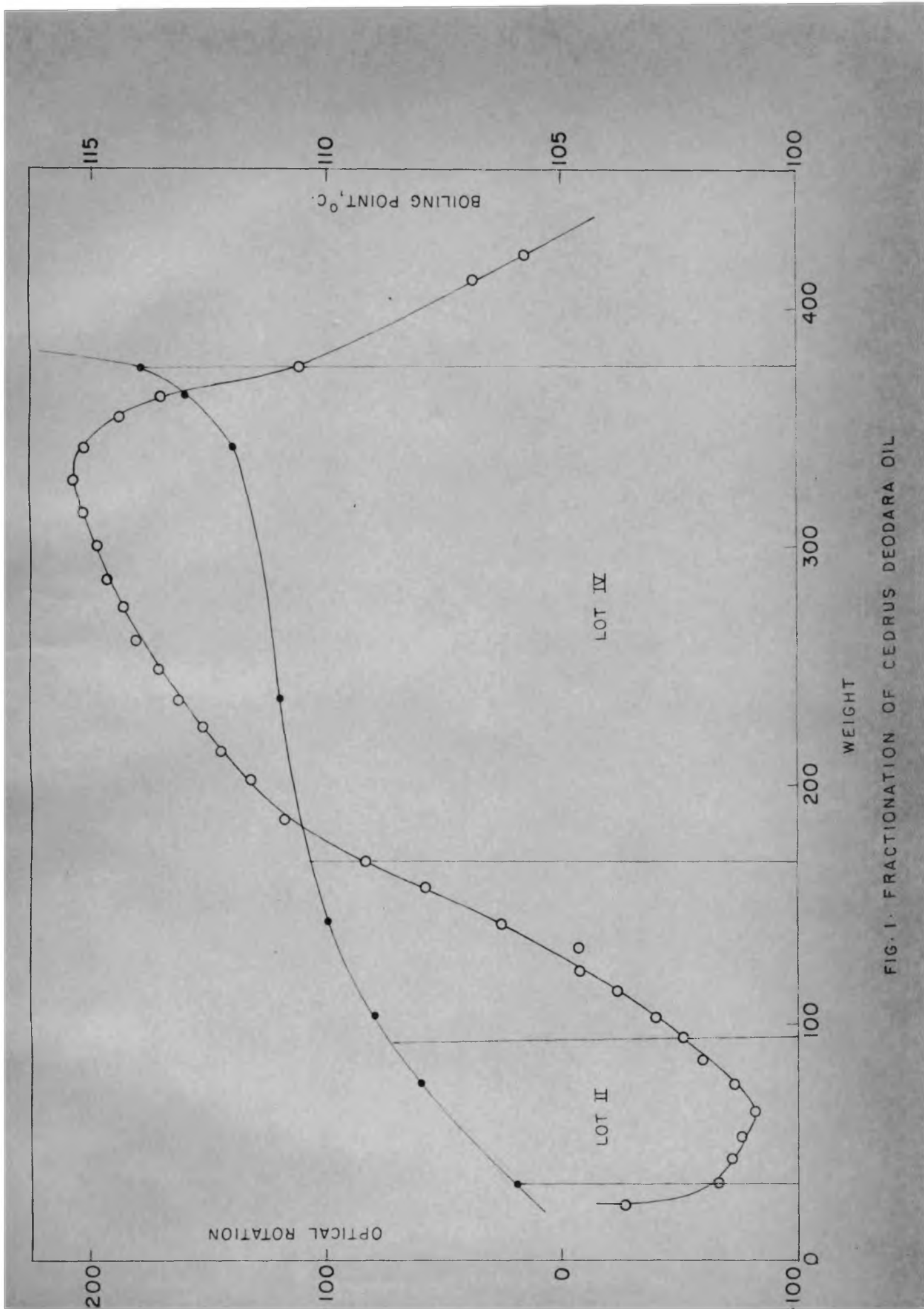


FIG. 1. FRACTIONATION OF CEDRUS DEODARA OIL

EXPERIMENTALFractionation of the essential oil:

Cedrus deodara oil (1760 gms) was fractionated carefully through a glass-helics 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 optical rotation of each cut. Cuts having almost same physical properties were mixed up and thus finally five fractions resulted (vide Table II). Given in Table II are the fractionation data for a typical experiment.

TABLE IIFractionation of Cedrus deodara oil

Fraction No.	Wt. (g)	b.p. **/mm	$[\alpha]_D$	Remarks.
1	22.75	85/5 - 106.5/5	-26.5°	Lot I, lower terpenes.
2	9.37	106/4	-67contd.

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

** Here the boiling points are somewhat lower ($\sim 8^\circ$) than those actually determined in the conventional apparatus for vacuum distillation, apparently because the location of the manometer in Emil Greiner assembly is such that the pressure recorded is nearer to the correct values.

TABLE II - continued.

Fraction No.	Wt. (g.)	b.p./mm	$[\alpha]_D$	Remarks.
3	10.08	110/5	-71.8) lot II) mainly) α -himachalene.
4	8.65	108 - 109/5	-75.6	
5	10.89	109/4	-81.6	
6	12.35	107 - 108/4	-72.8	
7	10.34	106/3	-59.4	
8	9.01	109/4	-52.1	
9	9.25	105/3	-40.0	
10	10.25	105/3	-24.32	
11	9.47	106/3	-8.46	
12	9.26	106.5/4	-7.16	
13	10.22	110/4	+25.5	
14	15.54	112 - 112.5/4	+58.68	
15	9.82	112 - 114/4	+92.74	
16	17.79	112 - 114/4	+118.54	
17	8.81	110/3	-	
18	9.26	113/4	+133.52	
19	10.17	113/4	+144.9) lot IV,) mainly) β -himachalene.
20	10.8	111 - 112/4	+151.8	
21	11.18	111/4	+162.8	
22	12.29	110/3.5	+170.8	
23	12.52	110/3.5	+179.9	
24	13.93	110/4	+186.8	
25	12.55	110/4	+192.8	

TABLE II - continued.

Fraction No.	Wt. (g.)	b.p./mm	$[\alpha]_D$	Remarks.	
26	13.65	113 - 113.5/4	197.1) lot IV mainly β -himachalene.	
27	13.62	113/4	+202.7		
28	13.58	111/4	+207.8		
29	13.46	112/4	+202.8		
30	13.1	112 - 113/4	+188.2		
31	9.07	113/4	+170		
32	11.84	112/3.5 - 113/3	+112.7		
33	36.67	113 - 136/3	+87.9) lot V, mainly himachalol.
34	11.45	134 - 141/3	+16.3		
Residue	28 gms.				

Cuts (2 to 8) having a maximum negative rotation were mixed and were refractionated for α -himachalene. Similarly lot number IV (fractions 16 - 33) having maximum positive rotation was mixed and refractionated for pure β -himachalene.

α -Himachalene:

The α -himachalene fraction (lot No. II, 256 g.) was refractionated through the same column maintaining a higher reflux ratio (1 : 22).

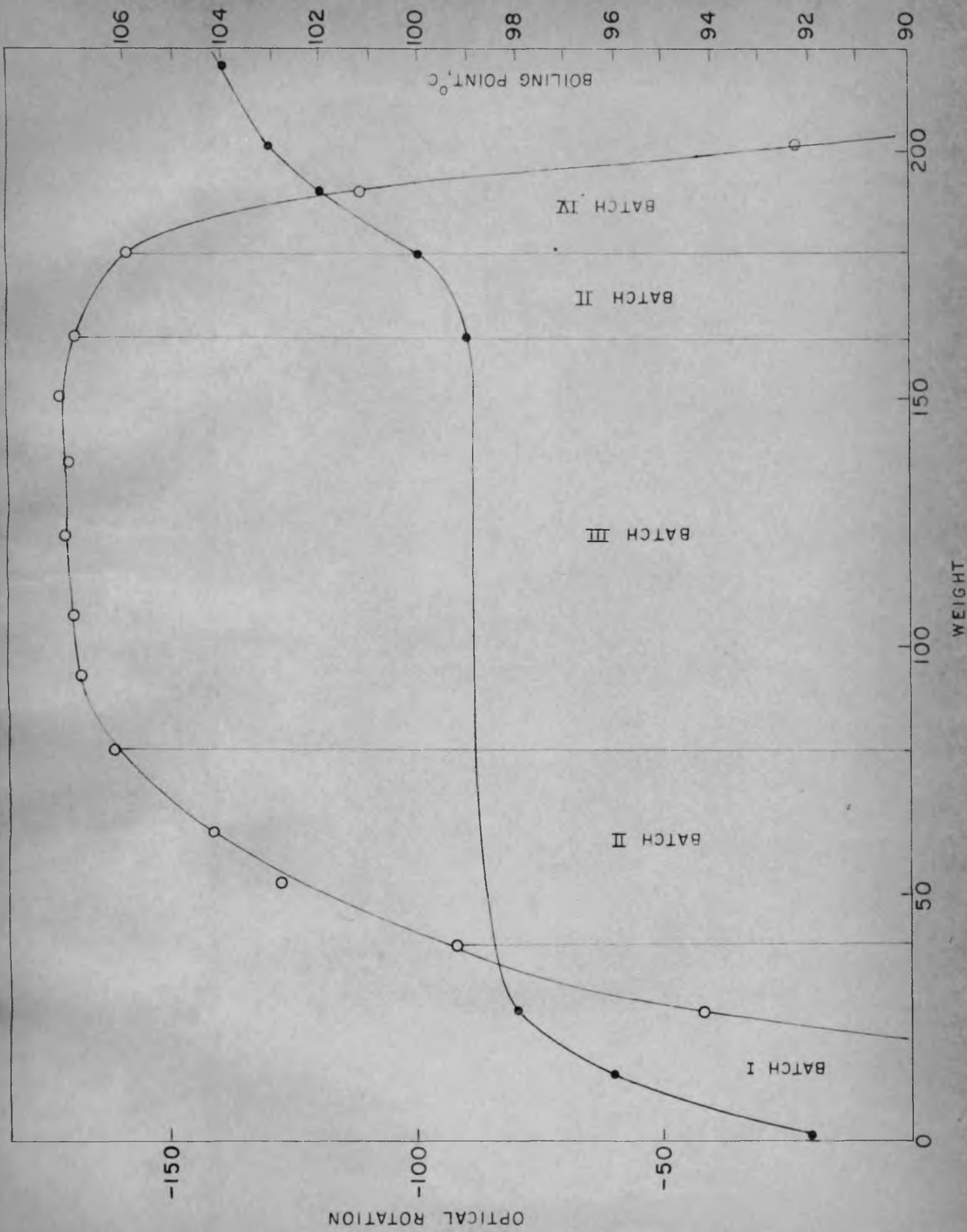


FIG. II. REFRACTIONATION OF α -HIMACHALENE

TABLE III
Refractionation of α -himachalene

Fraction No.	Wt.(g.)	b.p./mm	$[\alpha]_D$
1	0.77	92/5	-
2	12.69	93 - 96/5	+30.8
3	12.6	96.5 - 98/5	-42.1
4	13.3	97 - 98/4	-32.1
5	12.05	99/5	-128.1
6	10.75	100/5	-141.3
7	15.25	100/4.5	-161.8
8	3.13	98/4	
9	12.00	98/4	-163.5
10	11.81	99/4.5	-170.0
11	16.40	100/5.5	-171.85
12	1.67	99/5	
13	13.53	99/5	-171.3
14	12.96	99/5	-172.9
15	12.18	98/5	-170
16	16.84	99 - 100/5	-159.8
17	12.42	100 - 102/5	-112.1
18	9.77	102 - 103/5	-23
19	15.42	103 - 104/5	+44.5
20	16.06	104 - 105/5	+123.4
21	13.47	105 - 106/5	+206.5

The fractions having almost identical properties were mixed up to get four batches of α -himachalene with different grades of purity (see Fig.II). They were distilled over sodium and stored in dark bottles in a refrigerator. Batch No.III, after distillation over sodium represents the purest α -himachalene and its properties are recorded in Table IV. It is a colourless, mobile liquid with a pronounced odour of the wood. [Found: C, 88.22; H, 11.77; $C_{15}H_{24}$ requires: C, 88.16; H, 11.84%].

TABLE IV

Physical properties of himachalenes

Properties	α -himachalene	β -himachalene
b.p.	93.5°C/2 mm	121 - 122°C/4 mm
Density	d_4^{25} 0.9206	d_4^{25} 0.9330
Refractive index	n_D^{25} 1.50825	n_D^{25} 1.5130
Optical rotation (pure liquid).	$[\alpha]_D^{25}$ -172.7°	$[\alpha]_D^{25}$ +225.8
Optical rotation (in chloroform)	$[\alpha]_D^{27}$ -192.3° (conc. 4.162%)	$[\alpha]_D^{25}$ +224.7 (4.76%)
Molar refractivity	65.85	65.71

 β -Himachalene:

The β -himachalene fractions [(lot No.IV) 782 g.] was subjected to precise refractionation exactly as was done for the α -isomer.

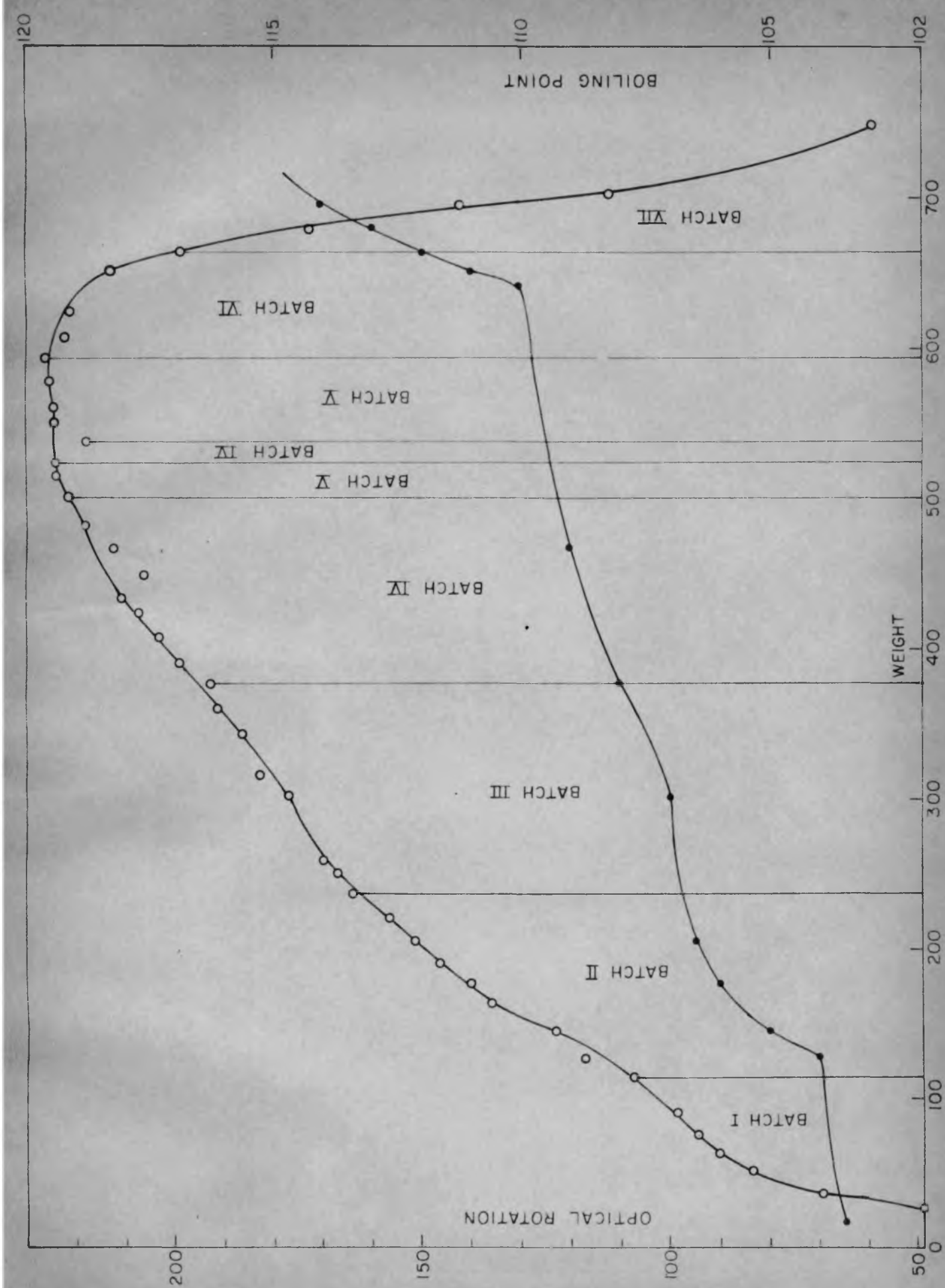


FIG. III. REFRACTIONATION OF β -HIMACHALENE

TABLE V
Refractionation of β -himachalene

Fraction No.	Wt.(g)	b.p./mm	$[\alpha]_D$
1	5.9	100 - 101.5/4	
2	11.66	103.5/4	+25.5
3	8.5	103.5/4	+49
4	12.47	103.5/4 - 104/3.5	+69.5
5	13.33	104/3.5	+83.4
6	10.15	104/3.5	+90
7	12.02	103/3.5	+94.4
8	16.1	103/3.5 - 103.5/3.5	+98.6
9	11.62	103/3.5	+96.7
10	12.15	104/4	+107.2
11	12.44	104/4	+117.1
12	16.57	105/4	+123.2
13	2.65		
14	16.82	104/3.5	+136.4
15	13.92	106/3.5	+140.2
16	14.85	106/3.5	+146.5
17	13.74	106.5/4	+151.4
18	15.55	106.5/4	+156.6
19	15.98	105/3.5	+164.4
20	13.05	105/3	+167.1

.....contd.

Fraction No.	Wt.(g)	b.p./mm	$[\alpha]_D$
21	8.55	105/3	+169.9
22	14.38	107/3.5	+162.5
23	14.15	"	+166
24	16.05	"	+176.7
25	18.36	"	+182.2
26	14.25	"	+181.6
27	13.49	"	+186.4
28	16.53	"	+191.6
29	15.05	108/3.5	+192.7
30	16.00	"	+198.9
31	15.76	"	+203.0
32	16.13	"	+207.3
33	11.2	"	+210.7
34	15	"	+205.7
35	17.45	109/3.5	+211.8
36	17.3	"	+217.86
37	16.7	"	+221.4
38	14.85	"	+224
39	8.27	"	+223.8
40	14.55	"	+217
41	13.55	"	+224
42	10.5	107/3.5	+224.4
43	16.20	"	+225.2

.....contd.

Fraction No.	Wt.(g)	b.p./mm	$[\alpha]_D$
44	14.77	108/4	+225.8
45	14.87	"	+221.8
46	16.65	109/4	+221
47	15.95	"	+218.5
48	9.53	111/4	+212.8
49	14.37	112/4	+199.2
50	15.9	113/4	+173
51	15.05	"	+142.4
52	6.35	114/4	+112.4
53 (Residue)	47	103 - 125/1	+59.4

The fractions having almost identical properties were mixed up to get seven batches of β -himachalene with different grades of purity (see Fig.III). They were distilled over sodium and stored in dark bottles at $\sim 5^\circ\text{C}$. Batch No.V, after distillation over sodium represents the purest β -himachalene and its properties are recorded in Table IV. It is a colourless mobile liquid, with an odour very similar to that of the α -isomer. [Found: C, 88.20; H, 11.79; $\text{C}_{15}\text{H}_{24}$ requires: C, 88.16; H, 11.84%].

Gas-Liquid Chromatography

Gas-liquid chromatography of the sesquiterpenes was carried out on a Perkin-Elmer Vapour Fractometer Model 154-D using different types of columns namely column K (polyethyleneglycol on diatomaceous earth), column P (succinic polyester of diethyleneglycol on celite) and column SDW (succinic polyester of diethyleneglycol on Chromosorb W). Hydrogen was used as the carrier gas. A typical analysis along with experimental conditions is shown in Figs. IV and V.

SUMMARY

Pure α - and β -himachalenes were isolated by careful fractionation of the essential oil of Himalayan deodar wood.

GAS-LIQUID CHROMATOGRAM

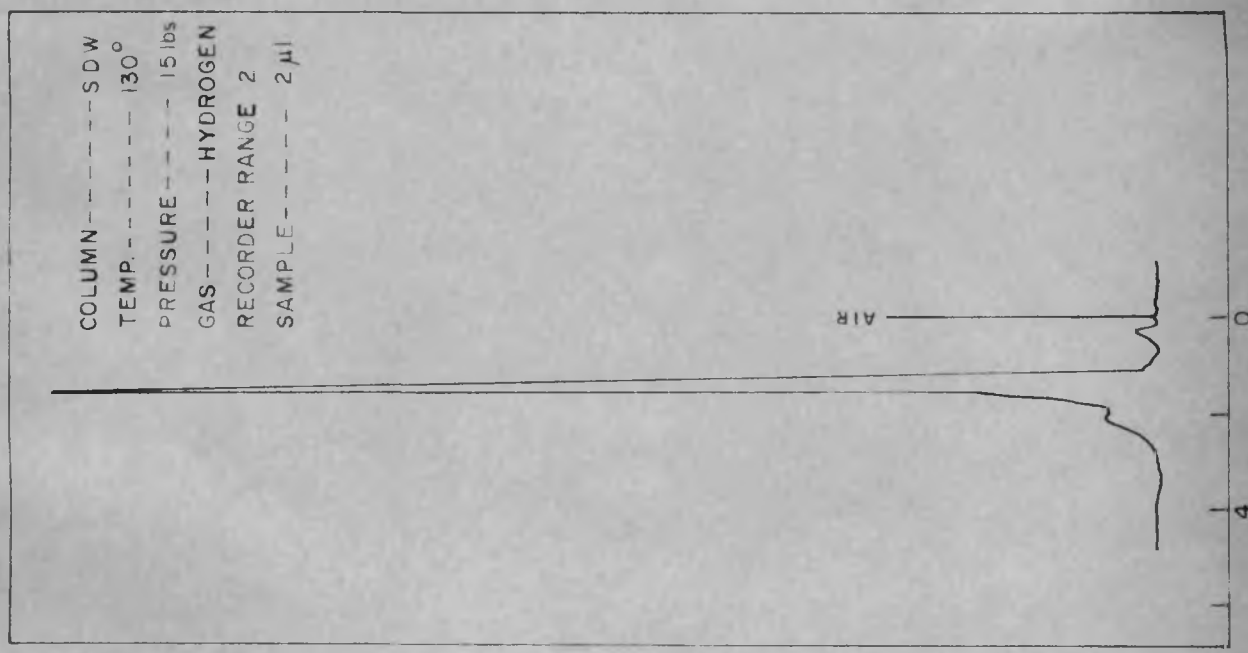


FIG IV α -HIMACHALENE

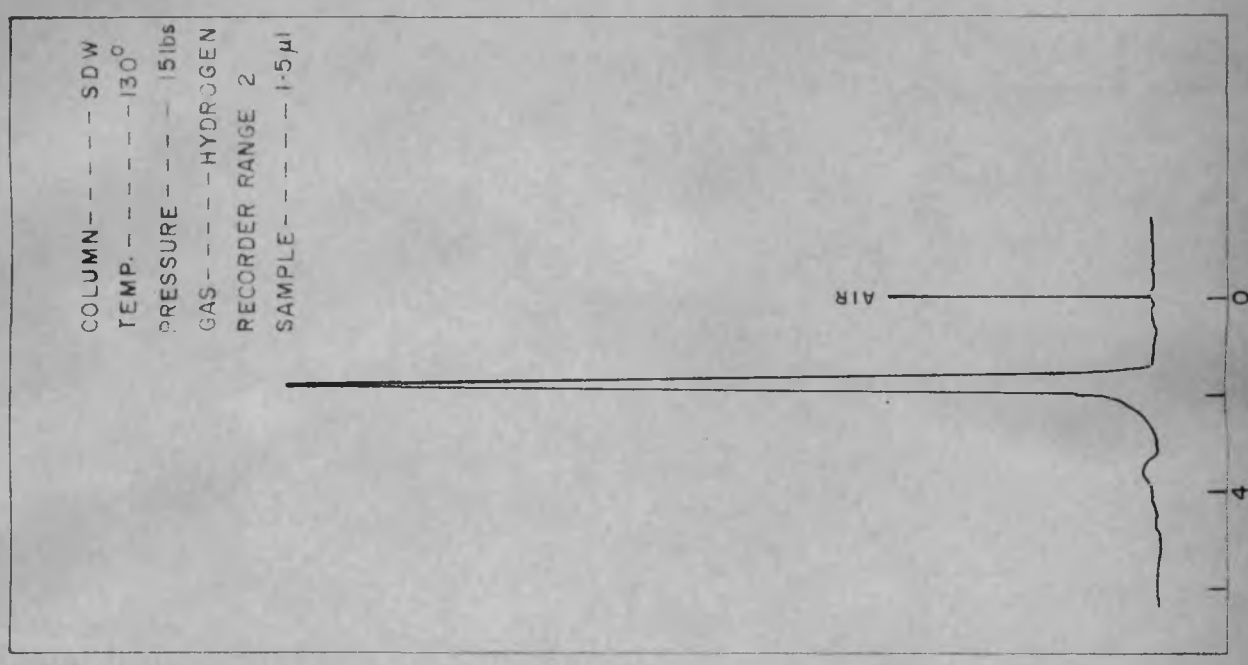


FIG V β -HIMACHALENE

REFERENCES

- 1 K.R. Kirtikar and B.D. Basu, "Indian Medicinal Plants" Vol. II, published by S.N. Basu, Allahabad (1918), p.1235.
R.S. Troup "The Silviculture of Indian Trees", Vol. III, Oxford, at the Clarendon Press (1921), p.1096.
- 2 The Drug Research Laboratories of Jammu and Kashmir Govt., Kashmir.
- 3 O.D. Roberts, J. Chem. Soc., 109, 791 (1916).
- 4 J.L. Simonsen and M. Gopal Rau, Indian Forest Records, 2, 123 (1922).
- 5 A. St. Pfau and Pl. A. Plattner, Helv. Chim. Acta, 17, 129 (1934).
- 6 L. Ruzicka, H. Schinz and P.H. Muller, Helv. Chim. Acta, 27, 195 (1944).
- 7 G.S. Krishna Rao, Sukh Dev and P.C. Guha, J. Indian Chem. Soc., 29, 721 (1952).