ON UTILISATION OF INDIAN TURPENTINE OILS

PART I

THE CONSTITUENTS OF TURPENTINE OILS FROM PINUS LONGIFOLIA ROXB, PINUS EXCELSA, PINUS KHASYA AND PINUS MERKUSII

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A perusal of the Indian Sea-borne Trade Journal will reveal that India purchases every year camphor of the value of about Rs 23 lakhs It is well known that camphor is manufactured on a commercial scale from α-pinene obtained from turpentine oil via bornyl chloride, camphene, *iso*bornyl-acetate, borneol The different operations involved in its manufacture have been the subjects of many patents and much literature (vide, Acharya and Wheeler, *J Univ Bom*, 1934, **3**, 153) In India, Acharya and Wheeler (*J Univ Bomb*, 1934, **3**, 153, 1935, **4**, 118) and Beri and Sarin (*Chem and Ind*, 1936, 605–607) by following the wellknown general methods mentioned above, converted α-pinene into camphor on a laboratory scale, the former authors used American turpentine oil as their starting material, and the latter used blue pine oleo-resin obtained from Rawalpindi

"One has to depend on *P longifolia* turpentine, as his source of pinene, at least for some time to come, because *Pinus excelsa* turpentine is neither being produced at present nor is there any likelihood of its being produced in the near future" This is the consensus of opinion of Kashmir, the Punjab and the U P forest officers

It is also well known that there is an unlimited supply of ordinary turpentine oil from *Pinus longifolia* in India

A systematic investigation has been undertaken in this laboratory with a view to finding out useful application of the ingredients of Indian turpentine oils, with special reference to that obtained from *Pinus longifolia* and its pinene content

In this part will be described the analyses of various turpentine oils e.g., *Pinus longifolia, Pinus excelsa* obtained from different parts of India, and *Pinus merkusii* and *Pinus khasya* procured from Burma

The only extensive source of pine oil in India is the oleo-resin from *Pinus longifolia* The constituents of this oil have already formed the subject of various investigations, and the relative proportions of the ingredients as reported by the previous workers are highly contradictory Rabak (*Pharm Rev*, 1905, **23**, 229), Schimmel (*Bull Imp Inst*, 1911, **9**, 8), Singh (*Ind Forest Rec*, 1912, **4**, pt. 1), and other workers established the presence of pinenes in this oil Afterwards Robinson (*Proc Chem Soc*, 1911, **27**, 247) proved the presence of α-pinene, β-pinene in it and predicted the presence of a new terpene which on treatment with hydrochloric acid gas gave sylvestrene dihydrochloride. It was Simonsen (*J C S*, 1920, **117**, 570) who found out the exact nature of this new terpene, and he proved the presence of **l**-α-pinene, β-pinene, a new dicyclic terpene named Δ^3-carene and also a new tricyclic terpene named longifolene. According to him the pinene content of the Indian turpentine oil is about 29 per cent, the rest being mostly Δ^3-carene and a small quantity of longifolene Watson (*J Indian Chem Soc*, 1926, **3**, 258) and his co-workers reported that only 8 per cent of pinenes could be obtained from this variety By applying the physical methods of analysis of the oil as devised by Darmois (*These de Doctorat Paris*, 1910), Dupont (*Ann Chim*, 1924, **10**, (1), 184) gave the following results of his analysis. **l**-α-pinene, 24 8%, β-pinene, 9 7%, *d*-Δ^3-carene + other constituent, 37 6%; oxidation products and longifolene, 20 3%, residue, 5 9% Besides the presence of Δ^3-carene he got indication of the presence of an isomeride of this terpene, and he supposed it to be Δ^4-carene Joffre (*Bull Inst Pin*, 1931, p 79) also confirmed the presence of an isomer of Δ^3-carene in the Indian turpentine oil

For our present analysis the turpentine oil from *Pinus longifolia* was obtained from the Government factory at Jallo in the Punjab. Repeated and careful fractional distillation revealed the presence of about 40% of α-pinene and β-pinene in the oil. But according to the analysis of Dupont the pinene content should be 34 5% This discrepancy perhaps can be explained as being due to our sample being of a higher quality, this assumption gets additional support from the fact that our sample contained only 5–7 per cent of oxidation products and longifolene, whereas, the oil examined by Dupont contained about 20 per cent of such products

In India there are many other species of pine yielding oils very rich in *α*-pinene, but at present the only extensive source of turpentine oil is that from *Pinus longifolia* The most serious defect about this oil is that it gets rapidly oxidised when exposed to air, due to the presence of large quantities of carenes in the oil

The following three varieties of turpentine oil have also been examined with special reference to their pinene contents, and the following are our results

1	*Pinus excelsa*, pinene content	87 0	per cent
2	*Pinus excelsa* (chakrata)	96 2	„
3	*Pinus khasya* pinene content	95 7	„
4	*Pinus merkusii* „ „	97 9	„

The oleo-resins of *Pinus khasya* and *Pinus merkusii* were obtained from the forests of Southern Shan State, Burma

It is worthwhile mentioning in this connection that turpentine oil obtained from the oleo-resin of *Pinus khasya* (Burma) gave about 96% of pinenes 76% (b p 150–55°) and 20% (b p 155–60°), whereas the oil from *Pinus khasya* (Assam) contained no pinene at all (*Bull Imp Inst*, 1917, **15**, 544–68), cf, however, Simonsen and Rao (*Ind Forest Rec*, 1922, **9**, 111–115) who found *α*- and *β*-pinene contents of the oil from *Pinus khasya* as 83 4%

The oil from the oleo-resin of *Pinus merkusii* (Burma) has now been found to contain about 98 per cent of pinenes without any trace of carene, whereas Simonsen (*Ind For Rec*, 1923, **10**, part 4) found it to contain about 85–87% (65 6%, b p 153–55°, 9 6%, b p 155–57°, 4 8%, b p 157–60°, 6 6%, b p 160–65°) of the pinenes and about 10% of carene

EXPERIMENTAL

Pinus longifolia.—The turpentine oil from *Pinus longifolia* used for analysis was obtained from the Government factory at Jallo. It was colourless and was found to have the following constants:

$$d_{22}^{22}=0{\cdot}8622,\ n_D^{27}=1{\cdot}4715,\ (\alpha)_D^{27}=-8{\cdot}29$$

Repeated fractional distillation of 4 kg. of the oil in an atmosphere of carbon dioxide gave the following fractions:—

No	B P (680 mm)	Per cent yield	d_{27}^{27}	n_D^{27}	$(\alpha)_D^{27}$	Remarks
1	153–55°	14	0·8575	1·4664	−20·99	α-pinene
2	156–58°	28·5	0·8574	1·4675	−15·64	α-pinene, β-pinene
3	158–60°	13·5	0·8587	1·4684	−8·39	β-pinene, Δ^3-carene
4	161–63°	13·2	0·8597	1·4691	−3·94	Δ^3-carene
5	164–68°	20·4	0·8599	1·4705	+1·77	Δ^3, Δ^4-carenes
6	168–70°	3·0	0·8604	1·4711	+2·17	carenes
7	Above 170°	5·0				longifolene
8	Loss, oxidation etc	2·4				

The fraction (1) on oxidation with potassium permanganate according to the method of G Galles et J Montanes. Anest Fisica Quim, 1930, **28**, 1163–64, gave pinonic acid, m p 64–65°.

The fraction (2) on oxidation with alkaline potassium permanganate, as above, yielded both pinonic acid, m p 64–65°, and nopinic acid, m p 122–23°C.

The fraction (3) was found to contain only a small quantity of β-pinene, identified by the formation of a little camphene on treatment with palladised charcoal.

The fraction (4) and (5) consisted of more or less pu carenes as they gave on treatment with nitric acid and amyl nitr in well cooled acetic acid solution, the nitrosate, m p 147 (decomp)

Pinus excelsa —The turpentine oil from *Pinus excelsa* w obtained from the Government factory at Jallo in the Punj It was almost colourless in appearance and had the followi constants

$$d^{26}_{26}=0\ 8595\ ,\quad n^{28}_{D}=1\ 4649\ ,\quad (\alpha)^{26}_{D}=+22\ 12$$

One kilo of oil on repeated fractionation gave the following fractio

No.	B P	Per cent. yield	d^{26}_{26}	n^{28}_{D}	$(\alpha)^{26}_{D}$	Main constituents
1.	150–52°	76 0	0·8559	1 4626	+24 59	α-pinene
2	153–55	7 8	0 8561	1 4628	+23 96	do
3.	120–190/30 mm	8·3				α-pinene, dipentene terpineol, sesquiterpe
4	Residue		6 0			
5	Loss		1·9			

The fractions (1) and (2) were found to be pure *d*-α-pinene T fraction (3) was obtained by distilling the residual oil left after t separation of fractions (1) and (2) under reduced pressure (30 mn yield 83 g This on refractionation at atmospheric pressure ga 64 g of oil boiling between 160–220° This fraction was found contain α-pinene, dipentene and terpineol , the higher boiling fracti contained mainly sesquiterpenes (cf Simonsen, *Ind For. Rec* , 19 **9**, 116)

The oleo-resin (42 lbs.) of *Pinus excelsa* obtained fro Chakrata in U P , on being subjected to steam distillation ga turpentine oil (10 2 lbs) This on distillation gave an oil (9·6 lb 22 8% on the weight of resin), of which 9 3 lbs distilled betwee 149–225°/680 mm , and 0 3 lbs between 115–190°/30 mm , leaving solid residue in the distilling vessel It was colourless and had th following constants: $d^{35}_{35}=0.8521$, $n^{35}_{D}=1.4600$, $(\alpha)^{35}_{D}=+42.10$ One kilo of oil on repeated fractionation gave the following fractions

No	B P	Per cent yield	d^{35}_{35}	n^{35}_{D}	$(\alpha)^{35}_{D}$	Main constituents
1	149–51°	90.2	0.8519	1.4611	+44.03	α-Pinene
2	152–54°	4.7	0.8458	1.4580	+39.73	do
3	155–60°	1.3	0.8368	1.4540	+35.31	do
4	161–225°	2.4				Terpenes
5	Loss with residue	1.4				

Pinus merkusii.—The oleo-resin of *Pinus merkusii* was kindly collected and sent to us by the Forest Economist, Utilisation Circle, Ahlone, Rangoon, (Southern Shan State, Burma)

30 lbs of the rosin of *Pinus merkusii* on steam distillation gave 6.4 lbs of turpentine oil (21.4%) on the weight of the resin. Two kilos of this oil on distillation gave 1.92 kg boiling at 149–55°/680 mm The residue yielded 41 g of oil when distilled under 30 mm pressure leaving a very small amount of solid residue in the distilling vessel The distilled oil was found to have the following constants

$$d^{26}_{26}=0.8561\,,\ n^{27}_{D}=1.4635\,,\ (\alpha)^{26}_{D}=-35.70$$

One kilo of the above oil on careful fractionation under 680 mm pressure gave the following fraction

No	B. P	Per cent yield	d^{26}_{26}	n^{27}_{D}	$(\alpha)^{26}_{D}$	Main constituents
1	149–51°	92.0	0.8559	1.4631	–35.70	α-pinene
2	152–54°	3.5	0.8564	1.4650	–36.09	do
3	155–58	2.4	0.8619	1.4670	–36.87	α-pinene, β-pinene
4	Residue with loss	2.1				

The fractions (1) and (2) consist mostly of pure l-α-pinene, the presence of β-pinene in fraction (3) was proved by the formation of nopinic acid on oxidation with alkaline permanganate

Pinus khasya —8 0 lbs of oleo-resin of *Pinus khasya* (kindly supplied by the Forest Economist, Utilisation Circle, Ahlone, Rangoon) on being subjected to steam distillation gave 621 g of oil, the yield being 16 8 per cent on the weight of the resin This oil on being distilled at atmospheric pressure (680 mm) gave 580 g of oil boiling between 150–70°C , and possessing the following constants

$d^{26}_{26} = 0\ 8589$, $n^{28}_{D} = 1\ 4649$, $(\alpha)^{26}_{D} = +15{\cdot}88$

500 G of the oil on being fractionally distilled gave the following fractions

No	B P	Per cent yield	d^{26}_{26}	n^{28}_{D}	$(\alpha)^{26}_{D}$	constituents
1	150–52°	83 2	0 8585	1 4645	+16·40	α-pinene
2	153–55	10 9	0 8590	1 4660	+10 21	do.
3	156–58	2 6	0 8637	1 4679	+ 5 23	β-pinene
4	Residue with loss	3 3				

The fraction (1) and (2) consisted mostly α-pinene, the fraction (3 being mostly β-pinene as it gave nopinic acid on oxidation wit alkaline permanganate

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