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A QUALITATIVE SURVEY OF PAKISTANI TURPENTINE OIL

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Abstract. Oleoresin samples from various compartments, and altitudes of Dadar, Batrasi and Kahuta forests were collected and steam distilled. The turpentine oil obtained was analysed using GLC. The yield of the oil varied from 15 to 24%; the pinene-content 43–69%; camphene 1–10%; Δ^3– carene, 26–52% and longifolene 0–12%. No direct relationship between the altitude and the pinene-content could be established.

Pine forests grow over a large area in the well-drained hilly ranges of the Punjab, North West Frontier Province and Kashmir. The commonest species is *Pinus roxburghii* (syn. *P. longifolia;* chir pines) growing at an altitude of 1200–1850 m. The other species are *P. gerardiana* Wall (chilgoza pine) and *P. wallichiana* (blue pine) growing at an altitude of 1850–3700 m. All the varieties of pine exude oleoresin, a process which can be accelerated by chemical,[1] biological[2] or physical[3] means. In Pakistan only *P. roxburghii* is tapped for the production of oleoresin employing physical means. This process consists of chopping off the bark 10–25 cm long and 1–1.5 m above the ground level. One cut or blaze is made on grade I trees (pole size; girth up to 40 cm), and two blazes are made on grade II trees (girth above 40 cm). The oleoresin begins to flow out at once into clay cups hung under the blazes. The resin is collected, transported to resin depots and then sent to rosin factories.

The oleoresin is subjected either to dry or steam-distillation when the turpentine oil distills over leaving behind rosin. 100 kg resin is said to yield 17.81 turpentine oil and about 75 kg rosin. The chief components of turpentine oil derived from *P. roxburghii* are α-pinene (I), β-pinene (II), Δ^3-carene (III) and longifolene (IV). Some other terpenes like camphene are also present in traces. The major use of tupentine oil is in paints and varnishes as a vehicle. It can also serve as a raw material for the manufacture of some important chemicals[5] such as terpene hydrate, terpineol, terpinolene, pine oil, camphor, camphene and menthol. For this purpose the pinene-content of turpentine oil is the decisive factor.[6]

Various studies on the Indian turpentine oil have been carried out in the past to determine its composition. In 1923 Simonsen[7] analysed Indian turpentine oil obtained commercially from the *P. longifolia* oleoresin and reported its composition to be I, 24%; II, 9.7%; III, 37.6% and IV, 20.3% and residue, 5.9%. Guha and Roy[8] examined the oil obtained from northern India and found high percentages of α and β-pinenes that is I, 40.0%; II, 17.6%; III, 18 8% and IV, 5.0%. A recent investigation carried out by Parbhakar *et al.*[9] reported α- and β-pinenes from 40 to 50%.

It is evident from these studies that the composition of turpentine oil obtained from *P. roxburghii* may vary from region to region. It is presumed that the quality may be dependent on various factors such as the altitude at which the tree grows, aspect of the forest, age of the tree, nature of the soil, season of tapping and the location of the blazes. No detailed studies were made to evalute the Pakistani turpentine oil. The present studies were undertaken to explore the quality of oil produced from various areas of our forests.

Experimental

Collection of Samples. Oleoresin was collected from Lehtrar and Tret forest ranges in the Punjab and Shinkiari and Batrasi ranges in the N.W.F.P. One sample each from grade I and II trees, growing within an altitude of 150 m, was obtained from each compartment. The compartments with higher altitude range were subdivided into upper and lower parts and then sampled. The samples were stored in well-stoppered tinned containers to avoid evaporation during transportation and storage.

Distillation of Turpentine Oil from Oleoresin. Because resin acids, on long contact at elevated temperatures isomerise, β-pinene to α-pinene,[10] steam distillation was used to obtain turpentine oil.

Oleoresin (200 g) was taken in 500 ml R.B. flask and subjected to steam distillation, the progress of which was observed from the appearance of oily drops in the condenser. The distillation was continued for another 20 min after the disappearance of oily drops. The whole process required about 2 hr. The distillate was transferred into a separatory funnel, saturated with NaCl and the oily layer removed. The oil was dried over Na_2SO_4 (an), filtered, weighed and stored. The yield of the oil on the basis of resin, is given in Table 1.

Analysis of Turpentine Oil. The oil samples were analysed by gas liquid chromatography on a Phase Sep LC2F apparatus with a flame ionization detector. A copper column 0.32 cm o.d. 2.75 m long and packed with 15% polyethyleneglycol succinate coated on 177–250 μ Chromosorb W; was used for separation with the oven temperature of 90. Nitrogen at a pressure of 1.4 kg/cm² was employed as carrier gas. A 2-μl sample of the oil was injected and the peaks were identified by the addition of known constituents. Areas under all the peaks were added together and

TABLE 1. COMPARTMENT-WISE YIELD AND COMPOSITION OF THE TURPENTINE OIL.

Compartment and altitude (m)	Elevation/ grade of trees		Percentage of Turpentine oil	α–Pinene	Camphene	β-Pinene	Δ^3–Carene	Longifolene	Total pinenes (α and β)
Dadar Forest (Shinkiari range)									
1/i 1146–1579	Lower	I	18·5	32·0	2·1	14·1	40·0	11·7	46·1
		II	15·0	31·0	1·3	13·8	51·7	2·1	44·8
	Upper	I	15·7	43·6	1·3	15·4	37·2	2·5	59·0
		II	21·0	34·6	1·8	23·1	37·5	3·0	57·7
1/ii 1174–1662	Lower and middle	I	17·1	38·6	1·7	20·0	36·3	3·3	58·6
		II	18·7	38·1	2·5	16·6	40·7	2·0	54·7
	Upper	I	19·0	41·7	2·5	17·6	35·3	3·4	58·7
		II	15·5	37·0	1·4	8·2	47·7	5·8	45·2
Batrasi Forests									
3/i 908–1219	Lower and middle	I	17·0	41·3	2·5	16·4	32·7	6·9	57·7
		II	17·5	45·0	1·7	17·2	35·0	1·2	61·2
	Upper	I	15·6	34·5	4·4	15·9	42·4	2·7	50·4
		II	16·4	44·1	1·1	15·5	35·4	3·8	59·6
		Mixed	17·3	41·8	2·8	17·5	32·5	5·2	59·3
3/ii 908–1100	Upper and middle	I	19·7	41·4	1·3	14·8	36·0	6·5	56·2
		II	15·1	33·9	2·2	21·7	33·9	8·4	55·6
		Mixed	16·0	43·5	1·3	15·8	37·6	1·9	59·3
Kahuta Forest (Lehtrar range)									
14/ii 1143–1372		I	17·4	40·4	2·0	17·4	36·2	4·0	57·8
		II	19·1	42·4	1·5	17·2	37·0	2·0	59·6
16 914–990		I	15·7	46·3	1·8	17·0	30·5	4·3	63·3
		II	17·2	37·9	3·0	14·5	40·3	4·3	52·4
18 884–1066	Middle and upper	I	16·9	50·8	1·8	13·6	31·4	2·1	64·4
		II	18·8	42·6	3·8	18·1	31·6	3·8	60·7
40/i 1036–1372	Middle and upper	I	15·0	39·1	9·5	13·5	35·8	1·9	52·6
		II	18·1	32·4	3·9	19·7	42·0	1·9	52·1
40/ii 960–1143	Upper and middle	I	18·3	32·0	5·7	10·7	47·7	4·1	42·7
		II	19·2	39·1	4·9	14·4	39·8	2·6	53·5
41/ii 914–1307	Lower	I	18·8	37.3	2·1	18·7	39·4	2·4	56·0
		II	18·0	40·6	4·6	20·7	28·5	5·5	61·3
	Upper	I	17·0	42·6	2·2	17·6	32·7	4·5	60·2
		II	19·6	40·7	1·6	16·8	38·0	2·6	57·5
		Mixed	17·7	47·0	2·9	19·8	25·9	4·4	66·8
43/i 716–990	Middle	I	23·6	41·2	3·7	17·1	32·2	5·7	58·3
		II	17·5	43·1	4·2	17·8	29·8	4·9	60·9
		Mixed	19·0	40·2	2·6	16·2	37·8	3·1	56·4
43/ii 914–1308		Mixed	15·2	43·3	2·5	16·4	34·1	3·7	59·7
67 1372–1707	Lower	I	17·5	35·5	2·7	15·8	41·6	4·5	51·3
		II	13·4	40·9	1·4	13·7	40·1	3·8	54·6
	Upper	I	18·6	48·3	2·4	12·0	33·2	4·1	60·3
		II	23·3	41·5	2·8	14·6	36·6	4·4	56·1
		Mixed	16·0	40·9	4·1	16·4	34·1	4·3	57·3

(continued)

(Table 1 continued)

Kahuta Forest (Tret range)									
86/ii 1067–1280	Middle and upper	I	17·5	36·6	1·5	13·3	45·0	3·6	49·9
		II	15·3	39·0	4·7	12·3	42·8	2·3	51·3
86/iv 835–1280	Middle and upper	I	17·8	41·5	4·4	20·3	31·8	2·0	61·8
		II	16·4	32·4	2·2	11·9	52·2	1·3	44·3
87 823–1219	Lower	I	15·3	49·3	2·0	19·6	29·0	—	68·9
		II	20·0	38·4	2·5	14·8	40·5	3·8	53·2

the percentages of individual components calculated from their ratio to the total area. The results are given in Table I.

Discussion

The yield of turpentine oil from the oleoresin varies between 15–24% (Table 1). This is considerably higher than that obtained by the Jallo Rosin Factory (15%). The oleoresin is often subjected to dry distillation which should yield higher percentages of oil. The difference in the yields can be attributed to the way the oleoresin is collected and transported by the forest department. They use open tins whereas we used tins with tight lids.

The samples of oleoresin were collected from four different regions and they exhibit noticeable differences in the yield and quality of the oil.

Dadar Forest (*Shinkiari Range*). The oil derived from oleoresin of younger trees has a higher percentage of pinenes compared to the older ones. The yield of the oil and the pinene contents increase with the altitude. There does not seem to be any relationship between the yield of the oil and the pinene contents.

Batrasi Forests. It is claimed that these forests have most of the aspects being lunar in shape and hence are ideal with respect to chir crop. This does not seem to be case as far as the quality of the exudates is concerned. The percentage of turpentine oil in the oleoresin derived from these trees is average or even below average in certain cases. There is a tendency of higher percentages of oil in the resin of grade II trees. The pinene content of oil is also more in the case of grade II trees. Higher percentage of oil, richer in pinenes, was obtained from the mixed sample which was collected from the resin depot of compartment 3/ii. This indicates that there are some trees in the compartment which exude resin which is richer in oil and which in turn has higher pinene-content than the ones from whom samples were collected.

Kahuta Forests. (a) Lehtrar Range: This forest seems to yield oleoresin better both in quantity and quality. Grade II trees yield oleoresin having higher percentage of oil. However, the pinene-content in the oil from grade I trees is higher. There is no clear-cut relationship between the oil-content and its pinene-contents. It is significant to note that the lesser the percentage of oil the higher is its pinene-content. The yield of the oil does not bear any definite relationship with the altitude though in most of the cases resin obtained from low-altitude trees yields more oil the only exception being compartment 67 where the position gets reversed. The aspect of the forest does not seem to have much effect on the quantity or quality of the oil. Sample collected from the resin depot of compartment 41/ii shows a very high pinene-content compared to samples collected from individual trees. This again indicates that the overall quality of oleoresin from the compartment in question is better, hence the presence of better quality oleoresin producing trees.

(b) Tret Range: The younger trees (grade I) yield oil richer in pinenes as compared to grade II trees. The pinene-content of the oil is inversely proportional to the altitude of the trees.

Δ^3-Carene-content of the oil varies between 26–52% in the samples studied. This seems to increase at the expense of both α- and β-pinenes. The percentage of longifolene varies between 0–12. It increases at the expense of all other terpenes, i.e. Δ^3-carene and α- and β-pinenes. However, its percentage does not seem to have any relationship either with age or the altitude of the trees.

In majority of the samples studied the pinenes-content varies between 55–69%. Admittedly this is not a very extensive survey but the studies clearly show that the pinene-contents of the Pakistani turpentine oil are much higher than what has been reported so far.[4,7,9]

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