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Studies on the *Pinus* Species Growing in Sri Lankan Plantations

III. Composition of Turpentine of *Pinus caribaea* (var. Hondurensis) of the Erabedde Plantation

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Abstract : The physical properties of turpentine isolated from trees of the *Pinus caribaea* (var. Hondurensis) plantation at Erabedde were very similar to data reported previously. Studies on chemical composition showed that the major component was α-pinene (75% - 85%), while the second major component appeared to be β-phellandrene (10%—15%). Although there appears to be little seasonal variation when bulk samples are considered, the turpentine composition of individual trees varies not only between tapping cycles but also shows daily changes.

1. Introduction

The turpentines of *Pinus* species have been a subject of intensive research during the period 1940-1960.[7] Investigations on 94 species have been documented by Mirov[7] where determination of chemical composition had been carried out using fractionation, classical chemical analysis and I. R. spectroscopy.

The turpentines of most *Pinus* species (gum and wood) have also been extensively studied by gas-chromatographic techniques[1,2,6,7,8,9,10] the results of which closely agree with previous studies.

Investigations have also been carried out on *Pinus caribaea* using provenances in Nicaragua[4,7] Honduras[3,4] Cuba[13] and Fiji.[12] In these cases, α- pinene content has been found to be 53-67,[4,7] 56,[3] 62-71[13] and 66[12] percent respectively.

In this study, we report the chemical composition of turpentine from local plantations which have been found to contain a significantly higher α- pinene content.

2. Experimental

Turpentine was isolated by the methods described previously.[5]

2.1. Physical Properties. Specific gravity of turpentine was determined using the specific gravity bottle. Refractive index was determined using a Hilgert refractometer while optical rotation was determined using a Carl-Zeiss polarimeter.

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2.2. Gas Liquid Chromatography GLC analysis of turpentine was carried out using a Varian Aerograph Moduline Model 1700 Gas liquid chromatograph. In a typical experiment the following procedures were followed. Using the method reproducibility was within 2%.

Operating conditions for Varian Aerograph Moduline Model 1700 *Gas Chromatograph*

Stationary phase	—	10% carbowax 20 M on Chromosorb W. (AW) DCMS
Column length	—	3 m
Column diameter	—	3 mm
Column temperature-Initial	—	70°C
-Final	—	200°C
Programme rate	—	2°/min. from 70°to 90°C
	—	4°/min. from 90° to 200°C and then hold
Injector block temperature	—	200°C
Detector oven temperature	—	250°C
Detector type	—	FID
(i) Air	—	275 ml/min.
(ii) H_2	—	25 ml/min.
Carrier gas flow rate	—	30 ml/min. (Ar)
Chart speed	—	5 mm/min.
Sample size	—	0.1 — 0.15 μl

Identifications were made by peak enrichment techniques.

3. Results

3.1. The Turpentine Sample. Samples used were obtained by water distillation of the oleoresin, care was taken to completely distill the turpentine (4 hours distillation) and keep distillation conditions constant. This was found to be important as the early distillate contained more monoterpenes than the later fractions.

3.2. Physical Properties. The more important physical properties of turpentine isolated appear in Table 1: average values being indicated. These are very similar to values recorded previously.[7]

TABLE 1. Some Physical Properties of Turpentine of *Pinus caribaea.*

1.	α_D	–47.2
2.	Refractive Index	1.471
3.	Density	0.862 gcm^{-3}
4.	Colour	Colourless
5.	Solubility in water	0.3% v/v
6.	Boiling range	
	157–160°C	~ 60%
	160–163°C	~ 20%
	163–190°C	~ 10%
	Polymerised	~ 10%

Determinations 1 to 5 were carried out at 30°C. The above analysis was done on a bulk sample.

3.3. Composition of Turpentine.

Composition of turpentine was determined by GLC analysis. α— pinene was the major component of the turpentine. The average α—pinene content was approximately 75%—85%. β—phellandrene was the next largest constituent. The average composition (from bulk samples) is given in Table 2. However, composition was found to vary depending on a number of factors.

TABLE 2. Average Turpentine Composition of *Pinus caribaea*.

	1	2	3	4	5
α – Pinene	79.4	77.9	79.1	83.6	76.3
β – Pinene	3.1	3.6	3.2	2.6	3.3
α – Phellandrene	0.9	0.3	0.9	0.8	1.2
β – Phellandrene	14.2	11.3	13.3	10.0	14.5
Camphene	0.9	2.2	1.0	1.5	1.3
p- Cymene	trace	trace	0.3	trace	trace
Longifolene	0.9	0.5	0.3	0.6	0.6
Methylchavicol	trace	0.3	0.7	trace	0.4
Unidentified (Sesquiterpine?)	0.3	1.4	1.7	1.0	2.0

1, 2, 3, 4 and 5 refer to separate bulk samples taken on different occasions from 30-50 trees (each time) of the plantation at Erabedde. 1 July 1978; 2 June 1979; 3 May 1979; 4 Sept. 1978; 5 March 1979.

3.4. Variation in Composition of turpentine

3.4.1. *Variation between trees.* There is a significant variation in composition of turpentine from tree to tree (Table 3) and this was found to be so for all tapping cycles. α—pinene is always the major component but can be as high as 92% and as low as 50%.

TABLE 3. Variation of Turpentine Composition between different Trees

Code No. of Tree	α-pinene	β-pinene	α-Phellandrene	β-Phellandrene	p–cymene	limonine	Camphene	Longifolene	Methylchavicol	Unidentified
1	83.7	3.7	0.3	1.0	—	0.5	1.4	0.2	1.7	6.3
4	93.3	1.2	0.3	3.0	0.2	0.3	0.8	—	0.1	0.8
5	78.0	4.2	1.0	12.6	—	—	1.0	1.5	0.8	0.3
10	91.5	3.9	0.5	1.3	—	0.7	1.1	—	0.7	—
101	79.2	3.8	0.4	1.4	—	0.9	0.9	0.3	2.3	9.2
102	91.5	2.1	0.4	0.8	—	0.8	0.9	—	1.0	—
108	77.2	4.3	0.7	2.4	—	1.0	1.5	0.4	4.4	0.7
109	87.1	4.6	1.0	1.1	—	1.0	1.0	0.2	3.1	—
110	78.4	5.3	0.7	8.2	0.1	0.7	1.5	0.2	1.6	0.7
111	80.6	4.8	—	1.2	—	0.8	1.4	0.6	2.5	4.5
112	92.2	3.2	0.5	0.9	—	0.7	1.2	—	1.4	—
113	85.6	3.8	0.4	0.9	—	0.4	1.0	0.2	2.1	—
114	68.5	3.7	0.9	22.6	—	—	0.9	—	1.4	1.5
115	89.3	4.1	0.4	1.7	—	0.6	1.1	—	1.4	—
116	85.2	3.5	0.2	0.6	—	0.5	1.3	—	2.6	0.2
117	90.3	3.9	0.4	1.1	—	0.7	1.3	—	1.9	0.1

Analysis of the turpentine of trees giving significant yields of oleoresin in the September 1978 tapping cycle.

3.4.2. *Variation during 'Seasons'*. Composition of turpentine of individual trees was analysed during 4 tapping cycles. (1) Sept. 1978 (2) Dec. 1978 (3) March 1979 and (4) June 1979 and the composition of each tree was found not to be constant. During the June 1979 tapping cycle (good oleoresin flow) α— pinene content was at its highest (Table 4).

TABLE 4. Variation in α– Pinene Content in Individual Trees during Different Tapping Cycles

Code No.	Sept. 1978	Dec. 1978	March 1979	June 1979
101	79.2	81.2	72.9	85.8
102	91.5	70.8	67.3	71.8
106	—	83.4	87.6	91.6
108	77.2	86.0	79.0	81.5
109	87.1	86.3	80.1	89.0
110	78.4	81.5	38.1	65.9
111	80.6	89.2	81.1	91.7
112	92.2	88.5	88.2	93.6
113	85.6	—	84.7	82.4
114	68.5	52.3	76.1	70.0
115	89.3	68.3	78.0	74.7
117	85.2	—	—	84.2
118	90.3	—	78.4	89.2
119	—	—	—	87.2
120	—	—	87.4	90.8

–, Not Determined.

3.4.3. *Variation from day to day*. A single tree (No. 5) was studied further by investigating daily variations in composition. There was a varying trend in the fluctuation of α—pinene content, depending on the time of tapping. (Table 5). Results obtained showed that α—pinene content appeared to be constant throughout the month of June 1979. On the other hand, the results obtained in March of the same year showed that the final value for α—pinene content was higher than the initial one. Results of experiments of December 1978 gave a final value which was less than the initial one. Another significant feature was inverse relationship between β— phellandrene and α— pinene content.

TABLE 5. Daily Variation in α– pinene content during Different Tapping Cycles using a Single Tree

Tapping Day	α Pinene and β Phellandrene content		
	Dec. 1978	March 1978	June 1978
1	83.6 (9.6)	59.5 (22.2)	78.9 (12.8)
2	75.6 (16.9)	65.3 (19.5)	73.3 (18.9)
3	80.3 (13.1)	62.1 (23.0)	81.0 (13.4)
4	72.8 (18.3)	78.6 (14.8)	81.8 (12.8)
5	74.7 (17.3)	73.6 (18.8)	78.9 (15.1)

β – phellandrene content is given in parenthesis.

4. Discussion

These investigations revealed that the main components of the turpentine of *P. caribaea* (of the Erabedde plantation) were identical to the normal constituents of pine gum turpentine. Due to the above reason and in the absence of preparative GLC apparatus, the separation of individual components and their identification by spectroscopic and other methods were not considered vital and as a result identifications were confined to retention time and peak enrichment data.

The data obtained was interesting as α— pinene content was relatively high; being of the order 75%-85%. That this component was α— pinene was confirmed as it was possible to quantitatively convert α— pinene to α—terpeniol.[10] The only other component of significant quantity was β— phellandrene.

The average composition of bulk samples of pine turpentine did not show a marked seasonal variation. However, individual trees showed variation not only by season but also from day to day. The seasonal variation of turpentines is a subject of controversy. While reports to this effect have been made before, most authorities think that there is little seasonal variation in pine turpentine composition and that composition is dictated mainly by genetic considerations.[7] It must be noted however, that these conclusions have been mainly reached by the study of pines growing in temperate climes where there is a definite growing season.

Another point of interest is that there appears to be an inverse relationship between α—pinene and β—phellandrene content. The sum of these two components often being nearly constant, when individual plants were considered.

This study is of significance as individual trees containing α— pinene levels of around 90% have been identified which could be used as a source of seed material for future plantations.

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