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COMPOSITION OF XYLEM RESIN FROM FIVE MEXICAN AND CENTRAL AMERICAN *PINUS* SPECIES GROWING IN ZIMBABWE

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Key Word Index—*Pinus leiophylla*; *P. michoacana*; *P. montezumae*; *P. pseudostrobus*; *P. oocarpa*; Pinaceae; resin; turpentine; rosin; terpenes.

Abstract—α-Pinene was the major constituent of turpentine from xylem resin of *Pinus leiophylla, P. michoacana, P. montezumae, P. pseudostrobus* and *P. oocarpa.* Longifolene was present in variable amounts in all the species except *P. pseudostrobus*, and among the 22 turpentine constituents identified, longipinene, longicyclene, sativene and cyclosativene were always associated with the presence of longifolene. A few of the 87 trees sampled contained moderate or large amounts of β-pinene and Δ-3-carene. Amounts of isopimaric acid in the non-volatile fraction of the resin from *P. michoacana* and *P. montezumae* were much lower than those in the other species.

INTRODUCTION

Although the existence of a worldwide industry based on the production of turpentine and rosin [1, 2] has given commercial impetus to the analysis of resin from *Pinus* species, tropical pines have been less studied than those from more temperate regions. Furthermore, where such studies have been made [3–5] they have often been limited to an analysis of the volatile (turpentine) fraction of the resin rather than the non-volatile (rosin) part.

The number of *Pinus* species native to Mexico [6] is probably greater than for any other country and several have been widely planted as exotics for timber or pulp production. In the course of studies aimed at evaluating exotic pine species growing in Zimbabwe as secondary sources of resin for the local naval stores industry, compositional data have been acquired, reported herein, which extend existing knowledge of five species of Mexican and Guatemalan provenance origin.

RESULTS AND DISCUSSION

After separation into volatile and non-volatile parts, some 87 xylem resin samples from individual trees of *P. leiophylla* Schiede & Deppe, *P. michoacana* Martinez, *P. montezumae* Lambert, *P. pseudostrobus* Lindley and two provenances of *P. oocarpa* Schiede were submitted to gas chromatographic analysis, supported by GC/MS in the case of the turpentine fraction. Acid number and unsaponifiable matter were also determined for each of the rosin samples.

The turpentine of all five species (Table 1) was characterized by high α-pinene levels although there were sometimes a few trees within each group that contained moderate or large amounts of β-pinene or Δ-3-carene. Marked tree-to-tree variation has been observed before with some of these species [3, 7–9]. Longifolene was present in modest amounts in *P. michoacana* and *P. oocarpa*, occurring in all samples, and in some, but not all, of the *P. leiophylla* and *P. montezumae* samples; it was entirely absent in *P. pseudostrobus.* Of the minor constituents, the sesquiterpenes longipinene, longicyclene, sativene and cyclosativene, hitherto unreported in these species, were always associated with the presence of longifolene. Aliphatic hydrocarbons, reported by Smith [7] in a large proportion of trees of *P. pseudostrobus* but found to be absent in this species by Perry [8], were not detected. The outstanding feature of the resin acid composition (Table 2) was the smaller proportion of isopimaric acid in *P. michoacana* (mean 2.5%) and *P. montezumae* (5.8%) compared to the other species (10.6–19.6%), although figures for individual trees of *P. montezumae* were somewhat variable (traces–21.8%). Rosin analysis, therefore, clearly supports the close botanical relationship which exists between *P. michoacana* and *P. montezumae*, and the difference between these and, say, *P. leiophylla*, which is not evident from an examination of turpentine composition.

Gas chromatographic analysis of underivatized samples of rosin revealed the presence of small, but significant, amounts of neutral compounds in *P. leiophylla* and *P. oocarpa* samples and this was reflected in the mean values of acid number and unsaponifiable matter for these two species: 142.0 and 13.3% (*P. leiophylla*) and 145.4/146.3 and 14.2/14.1% (two provenances of *P. oocarpa*). These data do not make *P. leiophylla* or *P. oocarpa* attractive as commercial sources of rosin. In contrast, mean values of acid number were higher and unsaponifiable matter lower for the other species: 157.8 and 4.8% (*P. montezumae*); 160.6 and 4.8% (*P. michoacana*); 165.0 and 5.8% (*P. pseudostrobus*).

EXPERIMENTAL

Sample preparation. Resin was collected from 27-year old trees of *P. leiophylla, P. michoacana, P. montezumae* and *P. pseudostro-*

Table 1. Constituents of the turpentine from *Pinus leiophylla*, *P. michoacana*, *P. montezumae*, *P. pseudostrobus* and two provenances of *P. oocarpa* (% relative abundance)

Component	*P. leiophylla**		*P. michoacana**		*P. montezumae**		*P. pseudostrobus**		*P. oocarpa* I†		*P. oocarpa* II†	
	Mean‡	Range	Mean‡	Range	Mean‡	Range	Mean‡	Range	Mean‡	Range	Mean‡	Range
α-Pinene	92.8	89.4–96.0	85.9	77.3–92.6	89.7	61.7–96.5	75.4	33.8–94.9	82.3	65.0–88.5	68.4	3.9–84.3
Camphene	1.5	1.4–1.7	1.3	1.1–1.4	1.3	1.1–1.5	0.9	0.4–1.3	1.1	1.0–1.2	1.0	0.5–1.2
β-Pinene	1.4	0.8–4.3	1.5	0.9–3.4	4.8	0.8–25.5	4.1§	1.1–17.6	2.8	0.8–20.7	8.9	0.8–28.1
Myrcene/Δ-3-carene	0.8‖	0.6–1.2	1.8‖	0.7–3.5	0.9‖	0.6–1.6	15.2¶	0.6–56.0	0.5‖	0.4–1.1	6.4¶	0.4–65.6
α-Terpinene	—	—	—	—	—	—	0.2	0.0–0.7	0.1	0.0–0.1	0.1	0.0–0.8
Limonene	0.5	0.4–0.7	0.5	0.4–0.6	0.5	0.4–0.8	0.7	0.3–4.5	0.6	0.4–1.1	0.5	0.4–0.7
β-Phellandrene	0.4	0.1–1.6	0.2	0.1–0.3	0.8	0.1–5.9	0.4	0.2–0.9	0.3	0.1–0.6	0.5	0.2–1.0
γ-Terpinene	—	—	—	—	—	—	0.1	0.0–0.5	0.1	0.0–0.1	0.1	0.0–0.7
Terpinolene	0.1	0.0–0.1	0.2	0.2–0.3	0.1	0.1–0.2	1.0	0.1–3.5	0.2	0.1–0.4	0.6	0.0–5.6
Longipinene	0.1	0.0–0.3	0.3	tr–0.6	0.1	0.0–0.4	—	—	0.6	0.4–0.9	0.7	0.3–0.9
Cyclosativene	0.0	0.0–0.1	0.1	tr–0.2	0.0	0.0–0.1	—	—	0.2	0.1–0.3	0.2	0.1–0.3
Linalool	—	—	tr	0.0–tr	tr	0.0–tr	0.1	0.0–0.3	tr	0.0–tr	tr	0.0–tr
Longicyclene	0.1	0.0–0.3	0.3	tr–0.6	0.1	0.0–0.3	—	—	0.4	0.2–0.6	0.5	0.2–0.8
Sativene	0.1	0.0–0.2	0.2	tr–0.4	0.0	0.0–0.2	—	—	0.3	0.2–0.4	0.3	0.2–0.4
Bornyl acetate	0.1	0.0–0.4	—	—	—	—	0.1	0.0–0.8	—	—	—	—
Longifolene	1.4	0.0–4.5	6.3	0.6–12.9	1.0	0.0–5.2	—	—	7.1	4.0–10.6	7.8	3.4–10.9
β-Caryophyllene	—	—	0.1	0.0–0.6	0.0	0.0–0.4	0.4	0.0–0.9	0.1	0.0–0.5	0.1	0.0–0.4
cis-β-Farnesene**	0.1	0.0–0.2	—	—	—	—	—	—	—	—	—	—
Methyl chavicol	0.4	0.0–1.2	0.6	0.1–1.8	0.6	0.0–1.9	0.1	0.0–0.8	2.0	0.7–4.5	2.5	0.7–5.2
trans-β-Farnesene	—	—	—	—	—	—	0.1††	0.0–0.2	tr	tr–0.1	tr	tr–0.1
α-Farnesene**	—	—	—	—	—	—	0.1	0.0–0.3	—	—	—	—
Others	0.2	0.1–0.4	0.6	0.2–1.0	0.2	0.0–0.6	1.1	0.2–2.9	1.3	0.9–2.3	1.4	0.7–2.6

*Provenance origin: Uruapan, Mexico.

†Provenance origin: Guatemala, low altitude (800 m) I; high altitude (2000 m) II.

‡Mean of 9 trees for *P. leiophylla* and *P. michoacana*; 10 for *P. montezumae*; 21 for *P. pseudostrobus*; 20 for *P. oocarpa* I; 18 for *P. oocarpa* II.

§Mixture with sabinene.

‖Myrcene only.

¶Mainly Δ-3-carene; individual trees range from myrcene only (low values) to mainly Δ-3-carene (high values).

**Tentative identification.

††Mixture with α-humulene.

tr = trace (< 0.05%).

bus growing at Chisengu Forest, Zimbabwe (19°54′S, 32°53′E) and 10-year old trees of *P. oocarpa* growing at John Meikle Forest Research Station, Stapleford Forest, Zimbabwe (18°42′S, 32°55′E). Samples were obtained by drilling a hole in the tree at breast height, inserting a tightly fitting glass vial and leaving for a few days to fill with resin. Vials were topped up with water and refrigerated until required for analysis. Samples were hydrodistilled for 5 hr in a volatile oil apparatus and the distillate (turpentine) separated from the H_2O. The non-volatile residue (rosin) was ground and dried *in vacuo* over P_2O_5 immediately prior to analysis.

Turpentine analysis. Constituents were identified by GC retention data and GC/MS. Analytical GC: 3 m × 2 mm stainless steel column packed with 15% Carbowax 20 M on Chromosorb W-HP (80–100); N_2 at 30 ml/min; column temp. programmed 75–225° at 4°/min; injector temp. 225°; FID detector temp. 250°. GC/MS: capillary GC using 25 m × 0.22 mm bonded phase vitreous silica, BP 20 (Carbowax equivalent); He at1 ml/min; column temp. programmed 50–220° at 4°/min; column outlet led directly into ion source of VG Micromass 7070F operating at 70 eV ionisation energy; scan speed 1 sec/decade.

Rosin analysis. Acid number and unsaponifiable matter were determined using ASTM procedures (D 465-59 and D 1065-56 respectively). Resin acid composition was determined by GC of the Me esters under the following conditions: 3.35 m (or 2.9 m) × 2 mm glass column packed with 5% Versamide 900 on Chromosorb W-HP (80–100); N_2 at 30 ml/min; column temp. isothermal at 220°; injector temp. 360°; FID detector temp. 270°. Methylation was carried out *in situ* by pyrolysis (in the hot injector port) of the tetramethylammonium salts formed by adding 2 drops of 20% $Me_4N^+OH^-$ in MeOH to 10 mg rosin in 1 ml dry MeOH; 2 drops of phenolphthalein were added to check the presence of excess base. Acids were identified by retention data derived from authentic samples run on Versamide and DEGS (10%; 2.5 m × 2 mm glass; column temp. isothermal at 200°; other conditions as above). The degree of 'contamination' of the acids by neutral compounds was determined by the GC of underivatized samples.

Table 2. Resin acid composition (%) of *Pinus leiophylla*, *P. michoacana*, *P. montezumae*, *P. pseudostrobus* and two provenances of *P. oocarpa* rosin*

	P. leiophylla†		*P. michoacana*†		*P. montezumae*†		*P. pseudostrobus*†		*P. oocarpa* I‡		*P. oocarpa* II‡	
Component	Mean§	Range	Mean§	Range	Mean§	Range	Mean§	Range	Mean§	Range	Mean§	Range
Pimaric	4.2	1.6–7.3	7.4	4.6–11.2	6.9	4.8–9.6	4.2	1.9–7.5	8.0	6.0–11.1	8.6	6.6–11.3
Levopimaric/ palustric	29.4‖	21.6–41.7	42.7	33.2–59.5	38.7	25.2–49.2	42.6	33.5–56.3	35.1‖	23.8–40.3	36.2‖	25.7–43.7
Isopimaric	19.6‖	5.3–25.9	2.5	tr–5.3	5.8	tr–21.8	16.2	4.0–22.5	13.2‖	7.6–24.0	10.6‖	1.9–18.4
Dehydroabietic	14.8‖	11.9–20.4	15.7	11.1–21.2	15.7	9.4–22.9	11.6	6.5–19.3	12.5‖	7.0–17.8	12.5‖	6.4–18.2
Abietic	16.9‖	13.6–19.9	16.8	8.2–22.0	17.0	13.9–22.4	14.0	9.6–19.3	12.0‖	9.0–15.2	12.6‖	8.4–20.8
Neoabietic	9.9	7.3–13.9	9.5	4.2–12.9	11.1	4.6–16.4	6.3	2.0–8.3	9.6	5.3–15.4	8.5	5.9–14.2

*Analysed as methyl esters.

†Provenance origin: As for Table 1.

‡Provenance origin: As for Table 1.

§Mean of 9 trees for *P. leiophylla* and *P. michoacana*; 10 for *P. montezumae*; 23 for *P. pseudostrobus*; 20 for *P. oocarpa* I; 18 for *P. oocarpa* II.

‖Contribution from neutral compounds *ca* 3–4%.

tr = trace.

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