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COMPOSITION OF XYLEM RESIN FROM *PINUS WALLICHIANA* AND *P. ROXBURGHII*

JOHN J. W. COPPEN, JANET M. ROBINSON and A. N. KAUSHAL*

Overseas Development Natural Resources Institute, 56–62, Gray's Inn Road, London, WC1X 8LU, U.K.; * Department of Tree Breeding, Dr Yashwant Singh Parmar University of Horticulture and Forestry, Solan, India

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Abstract—Turpentine from *Pinus wallichiana* xylem resin contained around 90% α-pinene. In addition to small amounts of other terpenes, isomers of undecane, dodecane and tridecane were detected as minor constituents. In contrast, *P. roxburghii* turpentine contained significant amounts of α-pinene, β-pinene and Δ-3-carene, the latter (*ca* 50%) predominating. Several sesquiterpenes were identified for the first time in these *Pinus* species. Abietic and isopimaric acid were the major resin acids of both species but *P. wallichiana* alone contained lambertianic acid.

INTRODUCTION

Pinus wallichiana A. B. Jackson, blue pine, occurs throughout the temperate Himalayas from Kashmir to Bhutan but because of its high altitudinal range, 1800–3700 m, has generally been considered unsuitable for commercial tapping aimed at the production of turpentine and rosin [1]. Encouraging results from recent tapping trials [2], however, made it desirable to examine the composition of the resin from this species in terms of both volatile terpenes (turpentine) and non-volatile diterpene acids (rosin) in order to determine whether or not it has advantages over *P. roxburghii* Sarg., chir pine, at present the sole source of Indian gum naval stores. Prior to this study, the results of which are reported herein, only three constituents of *P. wallichiana* turpentine had been identified [3], while knowledge of resin acid composition related to cortical resin and needles rather than xylem resin [4].

RESULTS AND DISCUSSION

Samples of resin from individual trees of *P. wallichiana* and *P. roxburghii* were separately distilled and the volatile and non-volatile parts analysed by GC and GC/MS. Yields of turpentine from the resin averaged 29.3% (*P. wallichiana*) and 26.7% (*P. roxburghii*).

Mean turpentine composition and the range of values for individual trees for both species are shown in Table 1. For *P. wallichiana*, α-pinene was the dominant constituent (90.7%) making it an inherently valuable turpentine for the production of aroma chemicals [5]. The only other terpenes to exceed 1% were camphene (2.5%) and β-pinene/sabinene (2.1%). The presence of saturated aliphatic hydrocarbons in *P. wallichiana* turpentine is worth noting; in the absence of MS examination these would have gone undetected since they co-elute (with no discernible separation) with more 'normal' turpentine components under standard chromatographic conditions. The three hydrocarbons detected appear to be isomers of undecane, dodecane and tridecane with upper mean limits of *ca* 1, 0.1 and 0.4% respectively. Δ-3-Carene (50.6%) was the major constituent of *P. roxburghii* turpentine with α-pinene (22.8%) and β-pinene/sabinene (14.1%) the next most abundant constituents; the latter was quite variable amongst individual trees. These results are in accord with those reported previously for the main components of this species [6–8]; most of the minor components are reported here for the first time. The proportion of high-boiling components (eluting >20 min), principally longifolene, was greater for *P. roxburghii* than *P. wallichiana* (5.8% cf 2.9%).

Mean values of acid number, saponification number and unsaponifiable matter for the rosin were 168.8, 176.2 and 5.8% respectively for *P. wallichiana* and 174.7, 184.1 and 4.8% respectively for *P. roxburghii*. Resin acid compositional data are given in Table 2. As is often the case in pines, abietic acid was the major acid in both species but *P. wallichiana* contained much smaller amounts of pimaric (0.7%) and neoabietic (4.8%) acids than *P. roxburghii* (8.3 and 15.1% respectively), the difference largely being accounted for by the presence of lambertianic acid in the former. This rather rare acid has previously been reported in cortical resin and needles of *P. griffithii* McClelland (syn. *P. wallichiana* A. B. Jackson) [4].

EXPERIMENTAL

Sample collection. Resin was collected from individual trees of *P. wallichiana* (11 samples) and *P. roxburghii* (5 samples) growing in natural stands near Simla (Mashobra Forest) and Solan, Himachal Pradesh, respectively. All trees were >35 cm dbh and at least 70–80 years old.

Sample analysis. Distillations and turpentine and rosin analysis were carried out using methods described elsewhere [11]. Additionally, saponification number was determined using ASTM procedure D 464-59. Resin acids were identified by retention data derived from authentic samples [11] with the

Table 1. Constituents of the turpentine from *Pinus wallichiana* and *P. roxburghii* (% relative abundance)

Component	*P. wallichiana* Mean*	*P. wallichiana* Range	*P. roxburghii* Mean*	*P. roxburghii* Range
α-Pinene	90.7	87.4–92.2	22.8	15.6–29.7
Camphene	2.5	2.1–3.2	0.4	0.3–0.5
β-Pinene/sabinene/C_{11}†	2.1	1.1–5.1	14.1	3.3–34.9
Δ-3-Carene/myrcene‡	0.4	0.4–0.5	50.6	37.6–61.2
α-Phellandrene	—	—	0.1	0.1–0.1
α-Terpinene	0.1	0.1–0.1	0.4	0.3–0.4
Limonene	0.5	0.4–0.5	0.9	0.6–1.4
β-Phellandrene/C_{12}§	0.1	0.1–0.2	0.7	0.6–0.8
γ-Terpinene	tr	tr–0.2	0.5	0.4–0.6
p-Cymene	0.2	0.1–0.2	tr	tr–tr
Terpinolene/C_{13}‖	0.4	0.3–0.9	3.8	3.0–4.6
Longipinene	0.3	0.2 0.4	0.2	0.1–0.2
Cyclosativene	tr	tr–tr	tr	tr–0.1
Longicyclene	tr	tr–tr	0.2	0.1–0.2
Sativene	tr	tr–tr	0.1	0.1–0.1
Longifolene	0.6	0.3–0.8	3.4	2.7–4.5
β-Caryophyllene/terpinen-4-ol¶	0.5	0.3–0.7	0.2	tr–0.5
α-Terpinyl acetate	—	—	0.3	0.2–0.3
trans-β-Farnesene/α-humulene	0.1	0.1–0.2		
α-Terpineol/borneol	0.2	0.1–0.3	—	

* Mean of 11 samples for *P. wallichiana*; five samples for *P. roxburghii*.

† *P. wallichiana*: mixture containing β-pinene, sabinene and isomer of undecane. *P. roxburghii*: mixture containing β-pinene and sabinene.

‡ *P. wallichiana*: myrcene only. *P. roxburghii*: mainly Δ-3-carene.

§ *P. wallichiana*: mixture containing β-phellandrene and isomer of dodecane. *P. roxburghii*: β-phellandrene only.

‖ *P. wallichiana*: mixture containing terpinolene and isomer of tridecane. *P. roxburghii*: terpinolene only.

¶ *P. wallichiana*: mainly β-caryophyllene. *P. roxburghii*: terpinen-4-ol only.

tr = trace (< 0.05%).

Table 2. Resin acid composition (%) of *Pinus wallichiana* and *P. roxburghii* rosin*

Component	*P. wallichiana* Mean†	*P. wallichiana* Range	*P. roxburghii* Mean†	*P. roxburghii* Range
Unidentified acid‡	2.8	2.4–3.6	—	—
Pimaric	0.7	0.3–1.0	8.3	7.0–8.8
Levopimaric/palustric	9.7	6.6–12.1	13.5	11.1–15.8
Isopimaric	23.2	20.4–27.0	20.9	19.4–23.2
Lambertianic	20.5	15.7–23.9	—	—
Dehydroabietic	1.7	0.4–4.3	1.5	1.2–2.4
Abietic	31.5	27.6–34.0	37.5	35.6–39.3
Neoabietic	4.8	3.7–7.3	15.1	14.1–15.9

* Analysed as methyl esters.

† Mean of 11 samples for *P. wallichiana*; 5 samples for *P. roxburghii*.

‡ RR_t (relative to pimaric) 0.88 on Versamide; 0.86 on DEGS.

exception of lambertianic acid, which was identified from published data [10].

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