Phytochemistry, 1969, Vol. 8, pp. 869 to 872. Pergamon Press. Printed in England

MONOTERPENES, FATTY AND RESIN ACIDS OF *PINUS LAMBERTIANA* AND *PINUS MONTICOLA**

ARTHUR B. ANDERSON, RICHARD RIFFER and ADDIE WONG

University of California Forest Products Laboratory, Richmond, California

(*Received* 19 *November* 1968, *in revised form* 26 *December* 1968)

Abstract—The sapwood and heartwood of sugar pine (*Pinus lambertiana*) and western white pine (*Pinus monticola*) have been examined for monoterpenes, fatty and resin acids. The principal qualitative differences between the terpene composition are the presence of Δ^3-carene in significant amounts in sugar pine and its apparent absence in western white pine and the presence of *n*-decane in western white pine and its absence in sugar pine. While the seldom reported *trans*-cinnamic acid was found in each of these pines, the recently reported sugar pine resin acid, lambertianic, was not found in western white pine.

INTRODUCTION

THE CONSTITUENTS of the heartwood of genus *Pinus* have been investigated systematically by Erdtman, Lindstedt and others in an effort to obtain evidence for a classification of these plants on the basis of the chemical composition of the heartwood extractives.[1] Principal components studied in some sixty or so species of pines were the phenolic substances, and results indicated that it is possible to distinguish between pines belonging to the subgenera *Diploxylon* and *Haploxylon* by their phenolic patterns. Erdtman recently reported that the phenolics in *Pinus krempfii* Lecomte, a species of disputed affinities, is closely related chemically to *Haploxylon* pines and not to *Diploxylon*.[2]

The volatile constituents, particularly monoterpenes in the oleoresins of pines, have been extensively studied by Mirov,[3] who demonstrated that the pattern of distribution of monoterpenes in oleoresins of pines may often be used for taxonomic purposes. Recent studies by Joye and Lawrence on the resin acid composition of oleoresin and rosins from twelve pine species clearly indicate that the source of some oleoresins can be identified by their resin acid composition.[4] Drew and Pylant recently reported on the composition of the volatile terpenes from the wood of fourteen pine species.[5]

Only a few of the more than 100 species of pines have been systematically investigated for their terpenes and fatty and resin acids in both sapwood and heartwood. Accordingly, it was decided to investigate the pattern of distribution of all these compounds to ascertain whether additional chemical evidence could be brought to bear on pine systematics. The present

---

* Part III in the series "Chemistry of the Genus *Pinus*"; for Part II see *Holzforschung* **20**, 36 (1966).

[1] H ERDTMAN, *Pure Appl. Chem.* **6**, 679 (1963). See also H. ERDTMAN, in *Recent Advances in Phytochemistry*, Vol. 1, p. 36 (edited by T. J. MABRY, R. E. ALSTON and V. C. RUNECKLES), Meredith Corp., N.Y. (1968).

[2] H. ERDTMAN, B. KIMLAND and T. NORIN, *Phytochem.* **5**, 927 (1966).

[3] N. T. MIROV, *Composition of Gum Turpentines of Pines*, U.S. Dept. of Agr. Tech. Bull. 1239 (1961). See also N. T. MIROV *The Genus Pinus*, p. 486, The Ronald Press, N.Y. (1967).

[4] N. M. JOYE, JR., and R. V. LAWRENCE, *J. Chem. Engng Data* **12**, 279 (1967).

[5] J. DREW and G. D. PYLANT, JR., *TAPPI* **49**, 340 (1966).

report deals with the composition of the monoterpenes, free fatty and resin acids in the sapwood and heartwood of *P. lambertiana* and *P. monticola* both of which belong to the group *Strobi* of the subgenus *Haploxylon.*

RESULTS AND DISCUSSION

Table 1 gives the summary of the terpene analysis. One of the qualitative differences between these two species is the presence of *n*-undecane in *Pinus monticola* and its apparent absence in *P. lambertiana.* Mirov reported similar findings in the oleoresin turpentine from these two species[3]—and he indicated that the oleoresin of *P. monticola* contained 2 per cent *n*-heptane, which we did not detect in the samples examined. Another difference between these two species is the presence of Δ^3-carene in significant quantity in sugar pine, although at best it appears as only traces in western white pine. Similarly, γ-terpinene appears only in trace quantities in white pine although it is found in fair amounts in sugar pine. Drew and Pylant previously reported on the composition of the turpentine obtained from the wood of these two species, and our findings are in good agreement.[5]

TABLE 1. GLC ANALYSIS OF THE MONOTERPENES OF *Pinus* SPECIES

Compound	Relative retention time	Per cent composition			
		Pinus lambertiana		*Pinus monticola*	
		Sapwood	Heartwood	Sapwood	Heartwood
α-Pinene	1·00	14	55	68	69
n-Undecane	1·45	—	—	4	3
Camphene	1·49	6	tr.	4	3
β-Pinene	1·87	5	2	23	13
Δ^3-Carene	2·22	30	31	—	tr.
Myrcene	2·96	8	2	tr.	1
Limonene	3·32	10	5	tr.	7
β-Phellandrene	3·81	tr.	—	tr.	1
γ-Terpinene	4·58	8	tr.	—	tr.
Terpinolene	5·51	19	5	tr.	3

— Could not be detected; tr. $<0{\cdot}5$ per cent.

Table 2 summarizes the composition of free fatty and resin acids found in the sapwood and heartwood of the two species; Table 4 gives the yields of each. *trans*-Cinnamic acid, previously isolated from sugar pine heartwood, was again confirmed and it has now been found in western white pine.[6] It will be of interest to determine whether this acid is likewise found in the other members of the same subgenera *Haploxylon* and group *Strobi*, or whether it is widely distributed among the pines. Oleic and linoleic acids appear to be the predominant fatty acids in each species.

Perhaps the principal qualitative difference between these two related species is the presence in sugar pine, of lambertianic acid, which Dauben and German recently found,[7] and its apparent absence in western white pine. An additional difference appears to be the

---

[6] A. B. ANDERSON, *J. Am. Chem. Soc.* **74**, 6009 (1952).

[7] W. G. DAUBEN and V. F. GERMAN, *Tetrahedron* **22**, 679 (1966).

TABLE 2. GLC ANALYSIS OF FREE FATTY AND RESIN ACIDS OF *Pinus* SPECIES

		Per cent composition			
	Relative retention time	*Pinus lambertiana*		*Pinus monticola*	
Acid		Sapwood	Heartwood	Sapwood	Heartwood
trans-Cinnamic	0·23	2^{u}	4^{u}	1^{u}	1^{u}
Stearic	0·26	—	2	—	—
Oleic	0·31	27	16	13	8
Linoleic	0·39	23	15	10	11
Arachidic	0·43	4	2	4	3
Linolenic	0·53	3	2	tr.	tr.
Pimaric	1·00	tr.	—	tr.	tr.
Sandaracopimaric	1·13	1	2	3^{a}	3^{a}
Levopimaric/palustric	1·33	3	6	27	24
Isopimaric	1·45	6	15	11	20
Abietic	2·06	4	10	22	22
Dehydroabietic	2·15	2	4	2	4
Neoabietic	2·29	—	—	1	2
Lambertianic	2·32	10	18	—	—
Unidentified		15	4	6	2

— Could not be detected; tr. < 0·5 per cent; ^{u} confirmed by u.v. spectral analysis; ^{a} i.r. spectra indicated mixture.

TABLE 3. TLC ANALYSIS OF RESIN ACIDS AS METHYL ESTERS

Methyl esters	R_f of standard	Resin acid methyl esters prepared from extracts
Sandaracopimarate	0·25	—
Isopimarate	0·36	0·36
Levopimarate/palustrate	0·43	0·43
Lambertianate	0·48	0·48*
Pimarate	0·52	0·52
Abietate	0·56	0·56
Dehydroabietate	0·61	0·61
Neoabietate	0·65	0·65

* Sugar pine only.

TABLE 4. COMPOSITION OF PINE EXTRACT

	Per cent			
	Pinus lambertiana		*Pinus monticola*	
	Sapwood	Heartwood	Sapwood	Heartwood
Ether soluble	2·5	6·2	2·7	8·2
Neutral	89·9	79·2	82·3	77·2
Acids	10·1	20·8	17·7	22·8
Fatty acids	59	41	28	23
Resin acids	26	55	66	75
Acids unidentified	15	5	6	2
Total acids in wood	0·25	1·29	0·48	1·87

presence of neoabietic acid in western white pine and its possible absence in sugar pine. The principal resin acids common to both species appears to be isopimaric acid followed by abietic.

EXPERIMENTAL

Sample Preparation

Tree specimens used in this investigation were supplied through the courtesy of the Deputy State Forester, Department of Natural Resources, Division of Forestry, Sacramento, California. The butt cross-sections of 12 or more in. in length from three freshly cut sugar pine and three western white pine, were prepared for analysis as soon as received. 1-in. cross sections were cut from each bolt. Sapwood from each of the three disks was combined and ground in a Wiley mill. The entire ground sample was thoroughly mixed in a mechanical mixer and samples transferred to large capped jars and stored in a cold room. Heartwood from each of the three bolts was similarly prepared.

Preparation of Extractives

The volatile terpene fraction was obtained by exhaustive steam distillation of the sawdust and the volatile oil fraction collected submitted to GLC analysis. Sawdust was transferred to a Soxhlet and extracted for 24 hr with acetone. The acetone was removed and the residue thoroughly triturated with ethyl ether. The fatty and resin acids were recovered from the ether extract and methylated in the usual manner for subsequent analysis.[8]

Chromatography

GLC of monoterpenes was carried out as previously described.[8] GLC of fatty and resin acids as methyl esters was carried out as previously described.[8,9] In addition the unit was provided with a micro-collector and the resin acid methyl esters, so collected, were then additionally characterized by i.r. and/or u.v. spectra. TLC of resin acids as methyl esters was carried out as previously described.[10] The percentages of fatty, resin and unidentified acids (Table 4) were determined from the quantitative GLC analysis.

[8] A. B. ANDERSON, R. RIFFER, ADDIE WONG and L. A. YNALVEZ, *Wood Sci.* **1**, 12 (1968).

[9] F. H. M. NESTLER and D. F. ZINKEL, *Anal. Chem.* **39**, 1118 (1967).

[10] R. RIFFER and A. B. ANDERSON, *Holzforschung* **20**, 36 (1966).