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MONOTERPENES, FATTY AND RESIN ACIDS OF *PINUS PONDEROSA* AND *PINUS JEFFREYI**

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Abstract—The sapwood and heartwood of ponderosa pine (*Pinus ponderosa*) and Jeffrey pine (*P. jeffreyi*) have been examined for monoterpenes, fatty and resin acids. The composition of the fatty and resin acids is comparable in each species. The principal qualitative differences between these two species is the presence of the hydrocarbons *n*-heptane, *n*-nonane, and *n*-undecane in the steam volatiles from Jeffrey pine and their apparent absence in ponderosa pine.

INTRODUCTION

THIS is a continuation of our investigation on the composition of monoterpenes, fatty and resin acids in the genus *Pinus*[1] and deals with these components in the sapwood and heartwood of *Pinus ponderosa* and *P. jeffreyi*, both of which belong to the subgenus Diploxylon.

RESULTS AND DISCUSSION

Our terpene analyses are summarized in Table 1. Each of the constituents in Jeffrey pine reported here, except for α-phellandrene (tentative) was previously reported by Smith to be present in its oleoresin.[2] Similarly, the monoterpenes in the oleoresin from ponderosa pine indicated by Smith are the same as reported here.[3] Goldblatt and Burgdahl[4] and more recently Drew and Pylant[5] investigated the composition of the terpenes from the wood of ponderosa pine. Each of these investigators reported the presence of around 1% each of camphene and *p*-cymene, in addition to the compounds listed. We did not detect these compounds in the wood samples examined.

The principal qualitative differences between these two species is the presence of the hydrocarbons *n*-heptane, *n*-nonane, and *n*-undecane in Jeffrey pine, and their apparent absence in ponderosa pine. Mirov pointed this out long ago in his investigation of the terpene composition of the oleoresins from these two pines.[6] According to Shaw, the group Macrocarpae is composed of three pines: *Pinus Torreyana*, *P. sabiniana* and *P. coulteri*.[7] Mirov found that, chemically, group Macrocarpae is characterized by the presence of alkane

* Part IV in the series "Chemistry of the Genus *Pinus*"; Part III, *Phytochem.* **8**, 869 (1969).

[1] A. B. ANDERSON, R. RIFFER and A. WONG, *Phytochem.* **8**, 869 (1969).
[2] R. H. SMITH, *Forest Sci.* **13**, 246 (1967).
[3] R. H. SMITH, "Variations in the Monoterpene Composition of Ponderosa Pine Wood Oleoresins", U.S. Forest Ser. Res. Pap PSW-15, Pacific Southwest Forest and Range Experiment Station (1964).
[4] L. A. GOLDBLATT and A. C. BURGDAHL, *Ind. Eng. Chem.* **44**, 1634 (1952).
[5] J. DREW and G. D. PYLANT, JR., *TAPPI* **49**, 430 (1966).
[6] N. T. MIROV, "Composition of Gum Turpentines of Pines", U.S. Department of Agr. Tech. Bull. 1239 (1961). See also N. T. MIROV, *The Genus Pinus*, The Ronald Press Co., N.Y. 486 (1967).
[7] G. R. SHAW, *The Genus Pinus*, Arnold Arboretum Pub. 5, Cambridge, Mass. (1914).

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

Compound	Relative retention time	Percentage composition in *Pinus jeffreyi* Sapwood	*Pinus jeffreyi* Heartwood	*Pinus ponderosa* Sapwood	*Pinus ponderosa* Heartwood
n-Heptane	0·28	20	38	—	—
n-Nonane	0·66	3	—	—	—
α-Pinene	1·00	1	5	3	10
n-Undecane	1·45	—	6	—	—
Camphene	1·49	3	tr	—	—
β-Pinene	1·87	2	1	12	20
Δ^3-Carene	2·22	15	22	51	37
α-Phellandrene	2·79	—	2	—	—
Myrcene	2·96	6	tr	5	10
Limonene	3·32	11	7	24	17
β-Phellandrene	3·81	12	7	tr	1
γ-Terpinene	4·58	tr	tr	2	1
Terpinolene	5·51	11	1	3	4
Unidentified		16	11		

tr Indicates <0·5 per cent.

hydrocarbons—either heptane or undecane, and felt there were sufficient reasons, biochemical as well as morphological and genetic, to include *P. jeffreyi* in this group.[6] The Shaw classification puts *P. jeffreyi* in group Australes, which also includes *P. ponderosa*.

The composition of free fatty and resin acids found in the sapwood and heartwood of the two species is summarized in Table 2, while the quantity of each is given in Table 3. The composition of ponderosa pine resin acids has been previously reported by Riffer and

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

Acid	Relative retention time	Percentage composition in *Pinus jeffreyi* Sapwood	*Pinus jeffreyi* Heartwood	*Pinus ponderosa* Sapwood	*Pinus ponderosa* Heartwood
Stearic	0·26	—	tr	1	tr
Oleic	0·31	46	4	26	2
Linoleic	0·39	26	3	17	1
Arachidic	0·43	tr	tr	tr	tr
Linolenic	0·50	tr	tr	tr	tr
Pimaric	1·00	1	9	5	8
Sandaracopimaric	1·13	tr	2*	tr	2*
Levopimaric/ palustric	1·33	2	18	15	25
Isopimaric	1·45	4	9	5	10
Abietic	2·06	8	31	10	29
Dehydroabietic	2·15	5	13	7	5
Neoabietic	2·29	—	10	8	18
Unidentified		8	1	6	—

— Could not be detected; * i.r. indicated mixture; tr indicates <0·5 per cent.

Anderson[8] and by Joye and Lawrence.[9] We had tentatively identified one of the acids to be tetrahydroabietic acid (i.e. 1·8–2·7 per cent). Joye and Lawrence on the other hand reported that ponderosa pine wood rosin contains about 2·9 per cent sandaracopimaric acid. In our present examination, we found one of the resin acids methyl esters had a retention value of 1·13 (based on methyl pimarate = 1·00), identical to that of the authentic methyl ester of sandaracopimaric acid. However, when this same resin acid methyl ester was collected from the GLC preparation, the i.r. spectrum did not correspond to that of the authentic standard.

TABLE 3. COMPOSITION OF *Pinus* EXTRACTS

	Percentage composition in			
	Pinus jeffreyi		*Pinus ponderosa*	
	Sapwood	Heartwood	Sapwood	Heartwood
Ether-soluble extract	2·8	10·5	3·5	28·2
Neutrals	34	31	65	42
Acids	66	69	35	58
Fatty acids	72	7	44	3
Resin acids	21	93	50	97
Acids unidentified	8	1	6	—
Total acids in wood	1·8	7·2	1·2	16·4

Further, on TLC analysis of the mixture of resin acid esters, nothing could be detected at the R_f (0·25) of authentic sandaracopimaric acid.[1] In any case, if sandaracopimaric acid is present, it is apparently accompanied by an additional acid with identical retention value of 1·13 which may be one of the tetrahydroabietic acids or dihydroabietic acids. This conclusion also holds for the "sandaracopimaric acid" reported from Jeffrey pine. The composition of the remaining ponderosa pine resin acids listed in Table 2 is in good agreement with Joye and Lawrence.[9]

No qualitative difference appears between these two pines in composition of the fatty and resin acids (Table 2). Neither does there appear to be a marked quantitative difference. Nothing would suggest that these pines are, in fact, different, but rather suggest that they are closely related.

EXPERIMENTAL

Methods used for extraction and analysis were the same as those described previously.[1]

[8] R. RIFFER and A. B. ANDERSON, *Holzforschung* **20**, 36 (1966).
[9] N. M. JOYE, JR. and R. V. LAWRENCE, *J. Chem. Engng Data* **12**, 279 (1967).