

MONOTERPENES, FATTY AND RESIN ACIDS OF *PINUS EDULIS* AND *PINUS ALBICAULIS**

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Abstract—The sapwood and heartwood of pinyon pine (*Pinus edulis*) and whitebark pine (*P. albicaulis*) were examined for monoterpenes, fatty and resin acids. The principal qualitative differences between the terpene composition of these pines are the presence of limonene in pinyon pine and its apparent absence in whitebark pine, and the presence of α -phellandrene in whitebark pine and its possible absence in pinyon pine. Quantitatively, the principal difference appears to be the predominance of α -pinene in pinyon pine, and the high percentage of Δ^3 -carene in whitebark pine. Among acidic components, the main qualitative difference is the presence of $\Delta^8,15$ -isopimaric acid in pinyon pine, and its apparent absence in whitebark pine.

INTRODUCTION

THIS paper presents our further investigations on the composition of monoterpenes, fatty and resin acids in the genus *Pinus*.¹ The report deals with the composition of these components in sapwood and heartwood of pinyon pine (*Pinus edulis*) and in whitebark pine (*P. albicaulis*), both of which belong to the subgenus *Haploxylon* group Cembroides and Cembrae respectively.

RESULTS AND DISCUSSION

Table 1 gives the summary of the terpene analysis of the two pines. The oleoresin turpentine from pinyon pine was reported by Mirov to contain five terpenes, the predominating component being α -pinene, followed by Δ^3 -carene.² In addition to the compounds reported by Mirov we found α -terpinene and trace quantities tentative, of camphene, β -pinene and, β -phellandrene. Eight terpenes were shown to be present in whitebark pine, the major entity being Δ^3 -carene (74 %), which was likewise reported by Haagen-Smit to be present in the oleoresin of this species.³ α -Phellandrene was also found although apparently it is not present in pinyon pine; the latter contained limonene, which appears to be absent in whitebark pine. In addition to this possible qualitative difference, the principal quantitative difference between these two pines is the predominance of α -pinene in pinyon pine and the high percentage of Δ^3 -carene in whitebark pine.

Table 2 summarizes the composition of the free fatty and resin acids found in the sapwood and heartwood of the two species. Table 3 gives the yields of each extract. Oleic and linoleic acids appear to be the predominating fatty acids in each species. Small amounts of palmitic and behenic acids were indicated to be present in pinyon pine, while these acids could not be detected in the whitebark pine sample examined.

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

¹ A. B. ANDERSON, R. RIFFER and A. WONG, *Phytochem.*, 8, 873 (1969).

² N. T. MIROV and P. M. ILOFF, Jr., *Am. Pharm. Assoc. J., Sci. Ed.* 44, 424 (1955).

³ A. J. HAAGEN-SMIT, T. H. WANG and N. T. MIROV, *Am. Pharm. Assoc. J., Sci. Ed.* 39, 254 (1950).

TABLE 1. GLC ANALYSIS OF WOOD MONOTERPENES IN *P. edulis* AND *P. albicaulis*

Compound	RRT	<i>P. edulis</i>		<i>P. albicaulis</i>	
		Sapwood (Percentage of total)	Heartwood (Percentage of total)	Sapwood (Percentage of total)	Heartwood (Percentage of total)
α -Pinene	1.00	45	71	2	7
<i>n</i> -Undecane	1.45	—	—	—	1
Camphene	1.49	tr	tr	tr	—
β -Pinene	1.87	tr	tr	5	5
Δ^3 -Carene	2.22	17	17	72	74
α -Phellandrene	2.79	—	—	20	1
Myrcene	2.96	6	2	—	1
Limonene	3.32	8	3	—	—
β -Phellandrene	3.81	tr	—	—	—
γ -Terpinene	4.58	6	3	—	6
Terpinolene	5.51	6	4	—	5
Unidentified		12	—	1	—

tr indicated <0.5 per cent.

— could not be detected.

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

Acid	RRT	<i>P. edulis</i>		<i>P. albicaulis</i>	
		Sapwood (Percentage of total)	Heartwood (Percentage of total)	Sapwood (Percentage of total)	Heartwood (Percentage of total)
Caprylic	0.02	—	—	tr	—
Palmitic	0.16	4	tr	—	—
Unidentified	0.18	3	1	—	—
Oleic	0.31	17	2	17	10
Linoleic	0.39	14	4	14	28
Arachidic	0.43	3	tr	8	7
Linolenic	0.50	—	tr	4	1
Unidentified	0.68	—	—	3	12
Behenic	0.71	4	1	—	—
Unidentified	0.88	—	—	4	4
$\Delta^{8,15}$ -Isopimaric	0.93	35	41	—	—
Pimaric	1.00	tr	—	4	2
Sandaracopimaric	1.13	3	6	1	tr
Levopimaric/palustic	1.33	2	10	11	8
Isopimaric	1.45	5	9	12	10
Unidentified	1.63	1	4	—	—
Abietic	2.06	9	2	13	12
Dehydroabietic	2.15	—	12	4	3
Neobietic	2.29	—	8	—	tr
Total of unidentified		4	5	12	19

— could not be detected.

tr indicates <0.5 per cent.

TABLE 3. COMPOSITION OF EXTRACTS OF *Pinus edulis* AND *P. albicaulis*

	<i>P. edulis</i>		<i>P. albicaulis</i>	
	Sapwood (%)	Heartwood (%)	Sapwood (%)	Heartwood (%)
Ether-soluble extract	3.2	4.6	3.6	6.4
Neutrals	31	42	52	66
Acids	69	58	48	34
Fatty	42	7	43	46
Resin	54	88	45	35
Acids unidentified	4	5	12	19

The composition of resin acids in pinyon pine reported here is in good agreement with the findings of Joye and Lawrence for the resin acids reported to be present in the resin of this species.⁴ Perhaps the principal qualitative difference between these two species is the presence of $\Delta^{8,15}$ -isopimaric acid in pinyon pine, and its apparent absence in whitebark pine. It will be of interest to determine whether $\Delta^{8,15}$ -isopimaric acid is also found in other members of the subgenera *Haploxylon*, or whether it is widely distributed among the pines.

EXPERIMENTAL

Methods used for extraction and analysis were the same as those previously described.¹ All specimens were collected and authenticated by the Deputy State Forester, Department of Natural Resources, Division of Forestry, Sacramento, California, and three specimens of each species were combined and investigated.

⁴ N. M. JOYE, JR. and R. V. LAWRENCE, *J. Chem. Engng Data*, **12**, 297 (1967).