

## MONOTERPENES, FATTY AND RESIN ACIDS OF *PINUS CONTORTA* AND *PINUS ATTENUATA*\*

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(Received 19 April 1969 in revised form 26 July 1969)

**Abstract**—The sapwood and heartwood of lodgepole pine (*Pinus contorta*) and knobcone pine (*P. attenuata*) have been examined for monoterpenes, fatty and resin acids. While eleven monoterpenes were identified as common to both species, the principal difference in the monoterpenes is in their major components, namely  $\beta$ -phellandrene (71 per cent) in lodgepole pine and  $\alpha$ -pinene (72 per cent) in knobcone pine. Four fatty acids and eight resin acids were identified as common to both species.

### INTRODUCTION

THIS study is a continuation of our investigation on the composition of monoterpenes and fatty and resin acids in *Pinus*.<sup>1</sup> The present report deals with the composition of these components in sapwood and heartwood of lodgepole pine (*P. contorta*) and knobcone pine (*P. attenuata*), both of which belong to the group Insignes of the subgenus Diploxylon.

### RESULTS AND DISCUSSION

Table 1 gives a summary of the monoterpene analysis. Each of the constituents in lodgepole pine reported here was previously reported by Smith to be present in its oleoresin.<sup>2</sup> Smith also reported the presence of sabinene, from traces to 2 per cent; this was not detected in wood samples we examined. More recently, Drew and Pylant investigated the composition of turpentine recovered from the wood of lodgepole pine and reported comparable findings except for the absence of limonene and the presence of 2.1 per cent of *p*-cymene which we did not detect.<sup>3</sup> Natural hybrids of *P. contorta*  $\times$  *P. banksiana* are found in Alberta, Canada, where they overlap.<sup>4</sup> These natural hybrids do not occur in California, from which our lodgepole samples were obtained, since the range of jack pine is far removed from California.

Bannister *et al.* reported on monoterpenes from the oleoresin of knobcone pine and identified five terpenes.<sup>5</sup> Our findings indicated two additional compounds: limonene (15 per cent), and terpinolene (7 per cent), together with traces of *n*-heptane,  $\alpha$ -phellandrene, myrcene, and  $\gamma$ -terpinene (tentative). Bannister likewise reported on hybridism involving *P. attenuata* and *P. radiata*. He found that while the two species differ markedly in the proportions of the major constituents,  $\alpha$ -pinene and  $\beta$ -pinene,  $F_1$  hybrids were, with one puzzling exception, intermediate. It was reported that Monterey pine averaged 73.0 per cent  $\beta$ -pinene, while the hybrid averaged 37.3 per cent  $\beta$ -pinene, and knobcone contained 3.2 per cent  $\beta$ -pinene.

\* Part VI in the series "Chemistry of the Genus *Pinus*". Part V, *Phytochem.*, in press.

<sup>1</sup> A. B. ANDERSON, R. RIFFER and A. WONG, *Phytochem.* 8, 869 (1969).

<sup>2</sup> R. H. SMITH, *Forest Sci.* 13, 246 (1967).

<sup>3</sup> J. DREW and G. D. PYLANT, JR., *Tappi* 49, 430 (1966).

<sup>4</sup> N. T. MIROV, *Composition of Gum Turpentine of Pines*, U.S. Dept. of Agr. Tech. Bull. 1239 (1961).

<sup>5</sup> M. H. BANNISTER, H. V. BREWERTON and J. R. C. McDONALD, *Svensk Papperstidn* 62, 576 (1959).

TABLE 1. GLC ANALYSIS OF WOOD MONOTERPENES

	RRT	<i>Pinus contorta</i>		<i>Pinus attenuata</i>	
		Sapwood (Percentage of total)	Heartwood (Percentage of total)	Sapwood (Percentage of total)	Heartwood (Percentage of total)
<i>n</i> -Heptane	0.28	tr	2	—	tr
$\alpha$ -Pinene	1.00	3	1	—	72
Camphene	1.49	1	1	14	4
$\beta$ -Pinene	1.87	1	tr	—	1
$\Delta^3$ -Carene	2.22	10	12	49	1
$\alpha$ -Phellandrene	2.79	12	3	—	tr
Myrcene	2.96	2	1	6	tr
Limonene	3.32	15	9	6	15
$\beta$ -Phellandrene	3.81	49	71	17	tr
$\gamma$ -Terpinene	4.58	1	—	—	tr
Terpinolene	5.51	5	—	—	7
Unidentified		1	—	8	—

— Could not be detected. tr Indicates <0.5 per cent.

Our findings for knobcone pine indicated 1.0 per cent  $\beta$ -pinene, which would suggest that no hybridism is involved here. The present analysis again confirms that the principal difference between these two species appears to be in their major monoterpene components, namely  $\beta$ -phellandrene (71 per cent) in lodgepole pine and  $\alpha$ -pinene (72 per cent) in knobcone pine. Mirov pointed this out long ago in his investigation of terpene composition of oleoresins from these pines.<sup>4</sup>

TABLE 2. GLC ANALYSIS OF FATTY AND RESIN ACIDS

Acid	RRT	<i>Pinus contorta</i>		<i>Pinus attenuata</i>	
		Sapwood (Percentage of total)	Heartwood (Percentage of total)	Sapwood (Percentage of total)	Heartwood (Percentage of total)
Oleic	0.31	9	16	7	2
Linoleic	0.39	5	12	3	1
Arachidic	0.43	2	2	tr	tr
Linolenic	0.50	—	1	tr	tr
Pimaric	1.00	3	5	5	4
Sandaracopimaric	1.13	2	1	1	1
Levopimaric/Palustric	1.33	5	14	19	17
Isopimaric	1.45	20	13	16	12
Abietic	2.06	18	10	20	36
Dehydroabietic	2.15	20	16	21	11
Neoabietic	2.29	—	4	8	16
Unidentified		16	6	—	—

— Could not be detected. tr Indicates <0.5 per cent.

Table 2 summarizes the composition of the free fatty and resin acids in the sapwood and heartwood of the two species; Table 3 gives the quantity of each. Four fatty acids and eight resin acids were identified as common to both species (Table 2). No qualitative difference appears between these two pines in composition of the fatty and resin acids. Neither does there appear to be a marked quantitative difference.

TABLE 3. COMPOSITION OF EXTRACTS

	<i>Pinus contorta</i>		<i>Pinus attenuata</i>	
	Sapwood (Per cent)	Heartwood (Per cent)	Sapwood (Per cent)	Heartwood (Per cent)
Ether soluble	3.9	3.6	0.52	2.3
Neutrals	45	38	43	24
Acids	55	62	57	76
Fatty acids	16	30	10	3
Resin acids	68	64	90	97
Acids unidentified	16	6	—	—
Total acids in wood	2.1	2.2	0.30	1.75

## EXPERIMENTAL

*Sample Preparation*

Tree specimens were obtained through the courtesy of the Deputy State Forester, Department of Natural Resources, Division of Forestry, Sacramento, California. The lodgepole pines were located near Battle River Reservoir, at 6000 ft elevation, Shasta County, California. The knobcone samples were selected from trees near the town of Shasta, Shasta County, elevation 1500 ft.

The butt cross-sections of 12 or more in. in length from three freshly cut lodgepole pine and three knobcone 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 were combined and ground in a Wiley mill. The three ground samples were combined and 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.

Methods used for extraction and analysis were the same as those described previously.<sup>1</sup>