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SHORT COMMUNICATION

TERPENOID CONSTITUENTS OF THE POCKET RESIN FROM COAST REDWOOD (*SEQUOIA SEMPERVIRENS*)*

RICHARD RIFFER, ARTHUR B. ANDERSON and ADDIE WONG

University of California Forest Products Laboratory, Richmond, California

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Abstract—The principal volatile component in the pocket resin of *Sequoia sempervirens* is α-pinene, while the major resin acids appear to be levopimaric and palustric acids among the five resin acids identified. Abietic acid could not be detected.

INTRODUCTION

ON OCCASION, open pockets in coast redwood (*Sequoia sempervirens*) heartwood contain reddish-brown blisters or beads of a very viscous, sticky resin. Preliminary examination of this material indicated that it contained terpenes, resin acids, and other constituents comparable to balsams and pine oleoresin. This is a preliminary report on the monoterpenes and resin acids.

RESULTS AND DISCUSSION

The gas–liquid chromatography (GLC) analysis of the volatile oil (5 per cent yield) recovered from the pocket resin is given in Table 1.[1] The major constituent is α-pinene, followed by limonene, with smaller amounts of β-pinene and myrcene. Each of these components was recently reported to be among the terpenes in the volatile oil from the foliage of coast redwood.[2]

Approximately 90 per cent of the pocket resin was soluble in aqueous sodium carbonate. This acidic fraction was methylated in the usual manner and submitted to GLC analysis.[1] Five resin acids were indicated (Table 2), which include levopimaric/palustric acids, isopimaric, a small amount of sandaracopimaric, and a trace of pimaric acid. Of interest here is the apparent absence of the abietic acids, since no peak was observed corresponding to abietic, dehydroabietic, or neo-abietic acids. Approximately 19 per cent of the total acidic fraction was unidentified, which included apparently some free fatty acids.

Additional evidence for the apparent absence of the abietic acids was indicated when the methyl ester mixture of the pocket resin was analyzed by TLC.[1] The only spots that were visible (Table 3) included levopimarate/palustrate (R_f 0·43) and isopimarate (R_f 0·36). No

* Part VII in the series "Chemistry of the genus *Sequoia*".

[1] A. B. ANDERSON, R. RIFFER and ADDIE WONG, *Phytochem.* **8**, 869 (1969).
[2] D. E. GREGONIS, R. D. PORTWOOD, W. H. DAVIDSON, D. A. DURFEE and A. S. LEVINSON, *Phytochem.* **7**, 975 (1968).

spot was visible corresponding to pimarate and sandaracopimarate, possibly due to the very small amounts indicated by GLC analysis. Because these latter acids were not confirmed, their identities remain tentative.

This is believed to be the first report of the occurrence of resin acids in the genus *Sequoia*.

TABLE 1. GLC ANALYSIS OF POCKET RESIN TERPENES OF *Sequoia sempervirens*

Compound	Relative retention time	Percentage of total
α-Pinene	1·00	77
β-Pinene	1·87	1
Myrcene	2·96	1
Limonene	3·32	21

TABLE 2. GLC ANALYSIS OF RESIN ACIDS OF *Sequoia sempervirens*

Acid	Relative retention time	Percentage of total
Pimaric	1·00	tr.
Sandaracopimaric	1·13	1
Levopimaric/palustric	1·33	57
Isopimaric	1·45	23
Abietic	2·06	—
Dehydroabietic	2·15	—
Neoabietic	2·29	—
Unidentified		19

tr. Indicates < 0·5 per cent. — could not be detected.

TABLE 3. TLC ANALYSIS OF RESIN ACIDS AS METHYL ESTERS

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

— Could not be detected.

EXPERIMENTAL

Preparation of Extractives

The reddish-brown resin in the pockets in coast redwood was removed with a glass rod and transferred to a glass vial. Several such collections were made over a period of time, transferring the pocket resins to the single vial, thus representing a composite sample.

The pocket resin, 2 g, was transferred to a 100 ml round-bottom flask and water added. A lighter-than-water oil trap with reflux condenser was connected to the flask. The mixture was refluxed until the volume of the volatile oil remained constant. The volatile oil fraction was withdrawn. Total yield was 100 mg or 5 per cent.

2 g of pocket resin was dissolved in ethyl ether and extracted several times with 10 per cent aqu. Na_2CO_3. The combined aqueous alkaline solutions were acidified with 10 per cent KH_2PO_4 and extracted with ethyl ether, which was then thoroughly washed with water. The liberated acids were esterified with diazomethane, using 10 per cent methanol in ether as the solvent. About 90 per cent of the resin was acidic.

Chromatographic analyses were carried out, as previously described.[1]