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The Constituents of the "Pocket Resin" from Douglas Fir *Pseudotsuga menziesii* (Mirb.) Franco*

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The pocket resin of Douglas fir, *Pseudotsuga menziesii* (Mirb.) Franco, has been investigated. The composition of this oleoresin is shown in Table 1. Resin acids of pimaric and abietic acid types were main constituents. Considerable amounts of resin acid methyl esters were also present. The main neutral constituent was a new diterpene alcohol, thunbergol, which is structurally related to thunbergene (cembrene), another constituent of the oleoresin.

The northern hemispheric genus *Pseudotsuga* of the order Pinales comprises about 7 species of which the North American Douglas fir, *P. menziesii* (Mirb.) Franco, is the most well-known. This species is also the only one which has been studied from a phytochemical point of view. It is a tall tree widely distributed in the mountainous ranges of the Pacific Coast from California to Oregon and further north. Two common varieties of this species are recognized, Coastal and Interior Douglas fir.

The wood of Douglas fir is used commercially and the wood extractives have therefore been subject to a number of investigations (*cf.* Ref. 1). In a more recent work Hancock and Swan [1] studied the light petroleum soluble extractives using modern chromatographic methods. They found that the total yield of extractives and the amounts of steam volatiles, fatty acids, resin acids, and unsaponifiables varied greatly between different trees and wood samples. They observed significant differences between Coastal and Interior varieties. The wood of the Interior variety contained larger amounts of the even-numbered C_{20}—C_{24} fatty acids than that of the Coastal variety. The main steam volatile wood constituents were α- and β-pinene, champhene, α-phellandrene, and β-cymene together with minor amounts of other common monoterpenes as well as a number of unidentified mono- and sesquiterpenes.

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Major constituents of the wood extractives were resin acids of the common abietic and pimaric acid types. Considerable amounts of fatty acids were also shown to be present. The neutral compounds obtained after saponification were glycerol and β-sitosterol together with some unidentified alcohols.

Because of wind shakes old trunks of Douglas fir often contain cracks or pockets which are filled with an oleoresin. This "pocket resin" is sometimes collected. The yield per tree usually varies from one to as much as 15 gallons. Surprisingly, very little was known about the chemical composition of this product.

There are some early investigations on the steam volatile part of the Douglas fir oleoresin. Schorger [2] reported the isolation of (−)-α-pinene and small amounts of (−)-limonene and (−)-terpineol from an oleoresin collected from heartwood whereas the steam volatile oil from the oleoresin of sapwood contained mainly (−)-β-pinene in addition to (−)-α-pinene and probably (−)-limonene. The volatile oil from "Oregon balsam" ("pocket resin") was shown by Benson and McCarthy [3] to contain approximately equal amounts of (−)-α-pinene and (−)-β-pinene. These two compounds constituted about 30 % of the crude material. The high boiling fractions were not investigated.

The present communication describes a detailed investigation of a commercial "pocket resin" (Western Crude Drug Company, Portland, Oregon, USA). The resin was dissolved in light petroleum and the neutral and acidic material separated by extraction with aqueous sodium carbonate according to the usual procedure. The acid fraction was esterified with ethereal diazomethane and analysed by thin layer chromatography and gas liquid chromatography according to a procedure previously described by Norin and Westfelt.[4] The fraction was shown to consist chiefly of resin acids of the common abietic and pimaric types. The composition of the fraction is shown in Table 1.

The neutral part of the resin was divided into crude "hydrocarbon", "aldehyde-ester" and "alcohol" fractions by chromatography on alumina. The various fractions were analysed separately by thin layer and gas liquid chromatography. The results of the analyses are summarised in Table 1. The relative amount of each constituent was estimated from the area of its gas chromatography peak. Some of the compounds marked with an *a* in Table 1 were separated by preparative chromatography and identified by direct comparisons with authentic samples.

The crude alcohol fraction contained an unknown compound in considerable amount. This fraction was therefore rechromatographed on silver nitrate impregnated silica gel to yield a colourless oily diterpene alcohol, $C_{20}H_{34}O$ (MW 290, mass spec.). The structural elucidation of this new macrocyclic diterpene alcohol, called thunbergol, will be described in the following paper.[5]

Thunbergol constitutes about 11 % of the pocket resin and is thus one of its main constituents. The corresponding hydrocarbon, thunbergene, which is a minor constituent of the resin, has previously been found in *Larix*,[7,8] *Picea*,[9] and *Pinus* [10,11] species and thunbergol appears to be closely related to "cembrol" [11] from *Pinus sibirica* L. Like the common resin acids these diterpenes seem to be rather common in *Pinaceae*.

Table 1. Constituents of Douglas-fir pocket resin.

Neutral material		%
Monoterpenes		
α-Pinene		6.7
β-Pinene		2.0
Δ^3-Carene		0.6
Limonene [b]		6.7
Terpineol [a]		5.6
Unidentified		1.6
Sesquiterpenes		
Longifolene [a]		0.2
Diterpenes		
Thunbergene [a]		1.8
Thunbergol [a]		11.4
Isopimarinal [a]		4.8
Resin acid methyl esters, total		3.6
Isopimarate	0.6	
Levopimarate / Palustrate	2.4	
Dehydroabietate	0.4	
Abietate	0.2	
Neoabietate	trace	
Unidentified	1.0	
	Total 46	

Acidic material	%
Resin acids	
Isopimaric	10.0
Levopimaric / Palustric	23.8
Dehydroabietic	1.6
Abietic	9.3
Neoabietic	7.3
Unidentified	2.0
Total	54

[a] Isolated on a preparative scale.
[b] *Added in proof.* Dr. E. Zavarin has kindly informed us that this constituent may be β-phellandrene or a mixture of limonene and β-phellandrene.

Surprisingly, the neutral fraction of the pocket resin contains resin acid methyl esters. There is only one previous report on a naturally occurring resin acid methyl ester namely methyl dehydroabietate which occurs in *Cistus labdaniferus*.[6]

EXPERIMENTAL

Thin layer chromatography (TLC) on silver nitrate impregnated silica ($AgNO_3/SiO_2$) was carried out according to a procedure previously described.[4] Unless otherwise stated gas liquid chromatographic (GLC) examinations were carried out on a deactivated silicon rubber (1 % E 301 on Gas-Chrom P) [4] column. The relative amounts of the various constituents were estimated from the areas of the GLC peaks (no corrections were made for differences in detector response of various constituents; hydrogen flame detector). Rotations were measured in chloroform (unless otherwise stated). Light petroleum refers to a fraction b.p. 40–60°.

Isolation of neutral and acidic fractions. The oleoresin (10.0 g) was dissolved in light petroleum and extracted with sodium carbonate (10 %, 3 × 100 ml). The combined aqueous solutions were washed with light petroleum, acidified, and worked up in the usual way to yield an *acid fraction* (5.4 g). The combined light petroleum solutions were dried (Na_2SO_4) and the solvent evaporated to yield an oily *neutral fraction* (4.6 g).

Investigation of the acid fraction. A small part of the acid fraction was esterified with ethereal diazomethane and analysed by means of TLC and GLC.[4] The following methyl esters were detected (% of total acid fraction): isopimarate (18.5 %), levopimarate + palustrate (44 %), dehydroabietate (3.0 %), abietate (17.3 %), neoabietate (13.5 %), and unidentified esters (3.7 %).

Investigation of the neutral fraction. The presence and amounts of α-pinene (14.6 % of the neutral fraction), β-pinene (4.3 %), Δ^3-carene (1.3 %), limonene (14.6 %), and terpineol (12.2 %) were determined by GLC of the crude neutral fraction.

One part of the neutral fraction (4.00 g) in light petroleum was adsorbed on alumina (neutral, activity II; 150 g). Elution with the solvents indicated gave the following fractions: (*1*) light petroleum (300 ml), 1.227 g; (*2*) light petroleum-benzene (1:1, 300 ml) 0.643 g; (*3*) benzene (300 ml), 1.042 g; (*4*) ether-benzene (1:1, 300 ml), 0.624 g; (*5*) ether (300 ml), 0.015 g.

Fraction (*1*) was distilled and the residue, b.p. above 110° at 100 mm Hg (20 %), was analysed by TLC and GLC. This residue was found to contain two main components: longifolene (0.4 % of the total neutral fraction) and thunbergene (3.9 %). The two compounds were separated on a preparative scale by chromatography on silver nitrate impregnated silica [4] and were found to be identical in all respects (IR, NMR) with authentic samples: longifolene, $[\alpha]_D$ + 48° (*c*, 1.5); thunbergene, m.p. 54—55°, $[\alpha]_D$ + 230° (*c*, 1.13).

Fraction (*2*) was found by TLC and GLC to contain a mixture of resin acid methyl esters and one further main component. The following methyl esters were detected: isopimarate (6.3 %), levopimarate + palustrate (25.6 %), dehydroabietate (4.2 %), abietate (2.5 %), and small amounts (~1 %) of neoabietate. The main constituent (50.2 %) of fraction (*2*) had a retention time identical with that of isopimarinal. This constituent was isolated by chromatography on silver nitrate impregnated silica [4] and had the following properties: $[\alpha]_D$ −12.2° (*c*, 1.0 in methanol); 2,4-dinitrophenylhydrazone, m.p. 181—182°, $[\alpha]_D$ + 108° (*c*, 0.8). The compound was identical with an authentic sample of isopimarinal.[12,13]

The presence of methyl esters in fraction (*2*) was also demonstrated in the following way: Part of fraction (*2*) (0.05 g) was heated with hydriodic acid (1 ml) and phenol (0.05 g) under reflux for 1.5 h. The evolved vapours were condensed to a solid at −80° (methyl iodide, m.p. −60°). After warming to room temperature this solid liquefied and was shown to consist solely of methyl iodide by GLC (10 % Carbowax 20M on Chromosorb W; column length 10'; temp. 40°).

Fraction (*3*) was analysed by TLC and GLC. Terpineol (8 % of the fraction) and an unknown compound (about 92 %) were main constituents. In order to isolate and characterize the unknown constituent fraction (*3*) (1.0 g) was chromatographed on silver nitrate impregnated silica (50 g); *cf.* Ref. 4). Ether-light petroleum (1:1) eluted a homogeneous oil ($[\alpha]_D$ + 75.4°; *c*, 0.63) which showed infrared bands at 3600 and 1100 cm^{-1} (CCl_4-solution) characteristic for a tertiary alcohol. Various attempts to obtain this alcohol in a crystalline state failed. The mass spectrum of the alcohol (thunbergol) exhibited a molecular peak at 290 *m/e*. (Found: C 82.1; H 11.9. $C_{20}H_{34}O$ (290) requires: C 82.7; H 11.8).

Fraction (*4*) was analysed by TLC and GLC and was shown to consist of almost pure terpineol.

Fraction (*5*) was shown to be a complex mixture by TLC. This minor fraction has not been further investigated.

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