

THE CHEMICAL COMPOSITION OF THE VOLATILE SEED OIL OF ENGELMANN SPRUCE (*PICEA ENGELMANNII*).

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ABSTRACT.—The volatile oil of the seeds of Engelmann spruce from central British Columbia was analyzed by gas-liquid chromatography and mass spectrometry. Twenty-three major and twelve minor terpenes, *n*-hexanal, *n*-hexanol, and several non-terpenoid trace components were identified. No noteworthy quantitative differences between the oils of four different seed lots were recorded.

The terpene patterns found in the volatile oils of the leaves, bark, and wood of conifers have been used extensively in chemosystematic studies (1,2). In contrast, those found in conifer seeds have not been investigated to any extent, the only recent study being that on the chemical composition of the seed oil of *Thujaopsis dolabrata* Sieb. et Zucc. (3). Part of the neglect may be owing to the restricted season in which fresh seed can be obtained, as well as to the difficulty of collecting large amounts in years of poor cone crops. Whereas the seeds of cedars and true firs may contain considerable amounts of volatile terpenes (4), little appears to be known about those of spruces or pines.

The present study was made on the volatile oil of four Engelmann spruce seed lots from central British Columbia, which were declared surplus owing to zero germination values.

RESULTS AND DISCUSSION

It has been found that hexane extraction and subsequent steam distillation (3) gives more reproducible results than direct steam distillation and that for gas chromatographic analysis on packed columns (1,2), at least 50 g seeds are required.

No noteworthy differences in the qualitative and quantitative composition (table 1) of these four seed oils were recorded, even though widely spaced Engelmann spruce populations from different elevations (800–1400 m.) were investigated. The yield of oil was very low (0.05 to 0.1%), making this seed oil less attractive

TABLE 1. Percentages of the major components of the volatile seed oil of Engelmann spruce, *Picea engelmannii* Parry.
(The four seed lots were from the North Thompson River district, British Columbia).

| Compound | % range | Compound | % range |
|---------------------------------------|-----------|--|---------|
| n-Hexanal..... | 5.5– 8.5 | Pinanone..... | 2.6–3.2 |
| α -Pinene..... | 13.0–15.0 | Borneol..... | 2.4–2.8 |
| Myrcene..... | 2.4– 3.6 | Terpinenol isomer..... | 1.2–1.8 |
| β -Pinene..... | 14.7–17.3 | Terpinen-4-ol..... | 3.3–5.1 |
| Car-3-ene..... | 0.7– 1.1 | Myrtenal..... | 1.1–1.5 |
| <i>p</i> -Cymene..... | 0.5– 0.7 | <i>p</i> -Cymenol } (α -Terpineol)..... | 4.5–8.5 |
| Limonene..... | 1.8– 2.1 | Myrtenol..... | 1.9–2.2 |
| β -Phellandrene..... | 3.0– 4.8 | Citronellol..... | 1.4–1.8 |
| γ -Terpinene..... | 0.8– 1.5 | Piperitone..... | 5.9–8.5 |
| Terpinolene..... | 0.5– 0.8 | Bornyl acetate..... | 0.8–1.3 |
| Linalool..... | 0.3– 0.7 | 2 isomeric } compounds } (parent ion } absent)(*) | 1.3–1.8 |
| Camphor..... | 1.6– 2.8 | | |
| Sabinene hydrate..... | 2.5– 3.5 | | |
| 2 isomeric } alcohols (MW152)..... | 1.0– 1.5 | | |

(*)The high retention times indicate these two isomeric compounds to be monoterpene acetates that lose the acetoxy moiety completely in the mass ionization process.

than, for example, leaf oil for the study of population differences. The chemical composition was more complex than that of the leaves, although most of the major terpenes are found in volatile oils of spruces (1). Unusual is the presence of relatively large amounts of *n*-hexanal, pinanone, myrtenal, myrtenol, and *p*-cymenol. Of the many minor (0.1 to 0.5%) and trace (less than 0.1%) components, *n*-hexanol, tetrahydrofuran, santene, α -thujene, benzaldehyde, camphene, sabinene, 1-octen-3-ol, 2-pentenylfuran, α -phellandrene, α -terpenene, 1:8-cineole, cuminic aldehyde, carvone, longifolene, two cadinol isomers, and manoyl oxide were identified by their mass spectra and retention times on the 30 m SP 2100 glass capillary column (5). The presence of traces of a diterpene hydrocarbon (MW 272), one diterpene alcohol with MW 288, four with MW 290, and manool was also indicated.

EXPERIMENTAL

PLANT MATERIAL.—Four Engelmann spruce (*Picea engelmannii* Parry) seed lots, No. 4271 (Mt. St. Anne, elevation 1410 m.), No. 4272 (Albreda River, elevation 890 m.), No. 4273 (Raft River, elevation 1060 m.), and No. 4274 (North Fork Creek, elevation 1370 m.) were collected in the North Thompson River seed zone of British Columbia during August 1979 and made available by the Duncan Seed Orchard of the British Columbia Forest Service.

DISTILLATION AND FRACTIONATION.—Aliquots of 10, 50, and 100 g of seed were directly steam distilled for 1, 2, and 4 hr respectively. Owing to severe "bumping" after $\frac{1}{2}$ to 1 hr, yields and relative percentages of the major components were not reproducible. Hexane extraction and steam distillation after removal of free acids (3) gave reproducible yields varying from 0.05 to 0.1% for the four different seed lots. Provided 50 g or more of seed were used, practically identical g c data were obtained.

ANALYSIS.—The volatile oils were analyzed on 3 packed g c columns (Apiezon L, polyethylene glycol-OV-17, PEG-QF-1 (6) on Hewlett-Packard model 5700A gas chromatographs (TC detector, helium carrier gas). The peak areas were integrated with a Hewlett-Packard model 3354A data system, and the relative amounts recorded on the 3 g c columns were averaged. Identification of individual components was carried out by the g c-mass spectral method described earlier (5), and they are listed in order of elution from the 30 m SP 2100 glass capillary column used in this method.

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