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The leaf oil terpene composition of incense cedar and coast redwood[1,2]

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This paper is dedicated to Prof. Raymond U. Lemieux on the occasion of his 60th birthday

E. VON RUDLOFF. Can. J. Chem. **59**, 285 (1981).

Analysis by an on-line computerized gas chromatographic – mass spectral method of the volatile leaf oils of the North American incense cedar and coast redwood revealed unusual percentage compositions of the major terpenes and presence of unique minor components. The chemosystematic implications are discussed briefly.

E. VON RUDLOFF. Can. J. Chem. **59**, 285 (1981).

L'analyse, par chromatographie en phase gazeuse couplée à une spectromètre de masse relié à un ordinateur, des huiles volatiles des feuilles du cèdre aromatique nord américain et du séquoia de mer révèle la présence de pourcentages inhabituels des principaux terpènes ainsi que la présence de constituants secondaires uniques. On discute brièvement des implications chimiosystématiques.

[Traduit par le journal]

Introduction

Recently, we reported on a gas chromatographic (gc) – mass spectrographic method for the identification of known terpenes in complex essential oils, such as the volatile conifer leaf oils (1). On-line computerized comparisons of mass spectra (ms) and relative retention times (rrt) facilitate quick and reliable assignment of peak identities even with the many terpenes that have similar ms. Of course the problem with unknown components, for which no reference spectra are available, remains. However, this is not a major drawback in chemosystematic studies because similarity or dissimilarity of unknowns with the same rrt in different or related species, varieties, hybrids, etc. can be established quite readily. We have improved this method by use of high efficiency glass capillary columns and although not all separation problems were solved, most components of several complex juniper leaf oils could be identified (2–4). The present communication deals with a similar analysis of the volatile leaf oils of incense cedar, *Calocedrus decurrens* (Torr.) Florin (syn. *Libocedrus decurrens* Torr.; fam. *Cupressaceae*) and for comparison also coast redwood, *Sequoia sempervirens* (D. Don) Endl. (fam. *Taxodiaceae*). Both sets of leaf samples were collected in the dormant season in northern California. The oil of incense cedar does not appear to have been analyzed by modern methods, whereas that of coast redwood was analyzed by gc and infrared (ir) spectroscopy by Levinson and co-workers in 1968 (5). Hilal *et al.* (6) reported on some bactericidal properties of redwood leaf oil components and the terpenoids of the pocket resin were investigated by Anderson and co-workers (7).

Results and Discussion

The mean relative percentage composition from 5 trees each of incense cedar and coast redwood is shown in Table 1. The terpene pattern of incense cedar is unusual among North American conifers, having relatively large amounts of limonene, car-3-ene, α-pinene, myrcene, and α-terpinyl acetate and low amounts of β-pinene, β-phellandrene, and the camphene group of terpenes (8). The presence of small amounts of 3-methylenebicyclo[3.2.1.]oct-2-ene, two possible isomers (rrt 0.252 and 0.394), and at least some of the 11 unknown minor components in the oxygenated monoterpene range is unique. The paucity of sesquiterpenes (no sesquiterpene hydrocarbon that may be correlated with Schorger's "libocedrene" (9) was found), but the presence of cedrol, as well as the absence of allyl phenyl ethers are also noteworthy. Trace components that could be identified were: tetrahydrofuran, oct-1-en-3-ol, *cis*- and *trans*-sabinene hydrate, borneol, *trans*-carveol, and methyl thymol. The quantitative variation from one tree to another was relatively small (8), although car-3-ene varied from 10 to 30%.

The major components of the leaf oil of coast redwood from northern California (α-pinene, limonene, β-phellandrene, γ-terpinene, myrcene, terpinolene, terpinen-4-ol, and eudesmol isomers) are the same as those reported by Levinson and co-workers (5). However, we found more sabinene than β-pinene, less α-terpineol and its acetate, and only traces of citronellol and geraniol. These dif-

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[1] Gas–liquid chromatography of terpenes. Part XXI. For part XX, see ref. 17.

[2] NRCC No. 18647.

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TABLE 1. The major (2% and more) and minor (0.2–2%) components of the volatile leaf oils of incense cedar (IC) and coast redwood (CR) from northern California

Compound	Relative retention time[a]	IC %[b]	CR %[b]
Hex-2-en-1-al	0.186	1.5	0.1
3-Methylene-bicyclo-[3.2.1]oct-2-ene	0.240	0.5	—
Unknown (MW120)	0.252	1.1	—
Tricyclene	0.316	0.2	0.1
α-Thujene	0.327	0.2	0.6
α-Pinene	0.338	9.2	24.9
α-Fenchene	0.358	0.6	—
Camphene	0.360	0.2	0.2
Unknown (MW120)	0.394	0.2	—
Sabinene	0.406	0.4	6.0
β-Pinene	0.411	0.5	1.8
Myrcene	0.446	8.0	4.7
α-Phellandrene	0.465	Trace	0.4
Car-3-ene	0.483	21.0	0.3
α-Terpenene	0.493	0.3	1.4
p-Cymene	0.502	0.2	1.2
β-Phellandrene	0.512	0.3	9.9
Limonene	0.159	31.3	8.6
trans-Ocimene	0.561	Trace	0.3
γ-Terpinene	0.578	0.8	6.2
Fenchone	0.609	0.5	—
Unknown	0.632	0.3[c]	—
Terpinolene	0.634	3.9	2.6
Unknown (MW150)	0.642	0.3	—
Linalool	0.667	0.3	0.1
Unknown (MW152)	0.709	0.3	—
Unknown (MW152)	0.713	0.2[c]	—
Unknown (MW152)	0.716	0.4[c]	—
Terpinen-4-ol	0.801	1.4	5.6
α-Terpineol	0.832	0.7	0.8
p-Cymenol	0.839	0.4	0.1
Unknown (MW150)	0.870	0.7	—
Piperitol	0.872	—	0.2
Unknown (MW152)	0.876	0.4	—
Unknown (MW180)	0.886	0.8	—
(Carvone)	0.906	0.7[c]	—
Unknown (MW152)	0.912	0.3[c]	—
Unknown (MW182)	0.916	0.4[c]	—
Piperitone	0.922	0.3	0.2
Unknown (MW182)	0.970	0.3	—
Bornyl acetate	1.000	0.5	0.4
Unknown	1.012	0.9	—
(Verbenone)	1.027	0.9[c]	—
Piperityl acetate	1.080	1.0	—
α-Terpinyl acetate	1.117	5.7	0.8
α-Copaene	1.182	—	0.5
β-Elemene	1.202	0.2	0.3
β-Caryophyllene	1.248	—	1.2
Humulene	1.304	—	0.3
Germacrene-D	1.347	0.2	5.5
α-Muurolene	1.378	—	0.3
α-Cadinene γ-Muurolene	1.413	—	1.6
Elemol	1.455	Trace	1.1
Elemol isomer	1.455	0.2	6.3
C_{15} alcohol (MW222)	1.494	0.2	—
Cedrol	1.530	0.8	0.1
γ-Eudesmol	1.582	0.1	1.8
β-Eudesmol	1.602	Trace	0.9
α-Eudesmol Cadinol isomer	1.612	Trace	2.5

[a] Relative retention time for bornyl acetate = 1.000.

[b] Relative percentages as obtained by integration and summation of peak areas.

[c] Impure.

ferences may be the result of variation from one population to another. In addition to the compounds listed in the table, we also identified trace amounts of isopentenyl isovalerate (an unusual hemiterpenoid ester found in yellow cedar, *Chamaecyparis nootkatensis* (D. Don) Spach (10) and Sitka Spruce, *Picea sitchensis* (Bong.) Carr. (11) leaf oils), hex-3-en-1-ol, tetrahydrofuran, oct-1-en-3-ol, 2-nonanone, 2-undecanone, *cis*-ocimene, *cis*- and *trans*-sabinene hydrate, camphene hydrate, borneol, neryl and geranyl acetate (but no citronellyl acetate), α-cubebene, β-bourbonene (like some of the cadinene–muurolene isomers a possible rearrangement product of germacrene-D (12)), thujopsene, β-selinene, β-cubebene, as well as several elemene, germacrene, cadinene and muurolene isomers, calamenene, 4:10-dimethyl-7-isopropylbicyclo[4.4.0]deca-1:4-diene (13), three cadinol isomers, torreyol, and possibly bisabolol. The elemol isomer with rrt 1.466 is not hedycaryol, the potential precursor of elemol and eudesmol isomers (14, 15), nor did its ms correspond to that of δ-elemol. At least 8 trace components in the monoterpene range and 15 in the sesquiterpene range remain to be identified. The great diversity of sesquiterpenes contrasts strongly with their paucity in incense cedar leaf oil and is, together with the relatively large amounts of the terpinene isomers, terpinen-4-ol, germacrene-D, and the elemol and eudesmol isomers, of chemosystematic value (8). Also, it is unusual in conifer leaf oils to find α-pinene as the main component, the only other North American species with this trait being the common juniper, *Juniperus communis* L. and yellow cedar (some trees only) (8).

Although not all of the leaf oil components of incense cedar and coast redwood could be identified, much data that are of chemosystematic value were readily obtained by the improved gc–ms method. Presence or absence of compounds of interest (even those with unknown ms) can be established without having to resort to more time-consuming separation techniques that require larger amounts of oil. By using the total ion count for each gc peak, relative percentages can be obtained simultaneously. These percentages correspond fairly well with those obtained with a thermal conductivity detector.

Incense cedar and coast redwood are monotypic species of the order *Cupressales* and their leaf oil patterns reflect their separate taxonomic classification. Whereas there is some similarity of the monoterpene hydrocarbon patterns with that of yellow cedar, the oxygenated monoterpenes and sesquiterpenes differ greatly (8, 10). Gough and Mills (16) have found unusual diterpenes in the wood of incense cedar.

Experimental

The leaves and twigs from 5 trees each of incense cedar near Gasquet and coast redwood east of Crescent City, northern California, were collected in the fall of 1977. These were transported and stored in the cold and dark. The leaves were separated from the twigs and steam-distilled for 6 h (4, 8, 17, 18). Whereas the recovery of volatile oil from coast redwood leaves was complete (0.4–0.7%, based on fresh weight), that of the incense cedar was incomplete and distillation was continued for a further 18 h (yield 0.6–0.9%). The relative percentages of the individual components were determined by analysis on four different packed gc columns (Apiezon-L, PEG 20M-OV 17, PEG 20M-QFI, and EGPN (17, 18); helium as carrier gas, TCD) (17–19). Aliquots (1 µL) of the leaf oils in ether (1:20 v/v) were analyzed by gc–ms on a deactivated 30 m SP 2100 glass capillary column (J + W Scientific) (1:30 split ratio, helium as carrier gas) on a Finnigan model 4000 quadropole gc – mass spectrometer (2), temperature-programming from 55°C (held for 6 min after injection) to 220°C (held for 15 min) at 3°/min. Mass spectral scans were taken every second. The recorded ms were compared by the computerized method (1) with those in our own file as well as the Finnigan Library of the National Bureau of Standards. Spectra of unknown compounds were also compared with those in the literature (e.g. ref. 13). The ms of peak 2 of incense cedar showed a "purity" of 900 (max. 1000) for 3-methylenebicyclo[3.2.1]oct-2-ene in the Finnigan NBS library, which represents a high degree of similarity. Mass spectrum of the elemol isomer: 121(100), 93(78), 41(71), 105(64), 67(61), 107(56), 91(52), 81(49), 79(44), 119(42) (just as with elemol, the parent ion peak mass 220 was not recorded); ms of sesquiterpene alcohol, rrt 1.530, *m/e*: 222(2), 95(100), 150(72), 43(63), 151(58), 41(51), 81(40), 93(35), 69(35), 107(33), 55(28). The ir and ^{1}Hmr spectra of the main components of incense cedar leaf oil were recorded for the fractions isolated in preparative gc (17–19).

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