Essential Oils of the Leaves of the *Raukaua* Genus (Araliaceae)

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The *Raukaua* genus of the family Araliaceae consists of 3 species, *R. anomalus, R. edgerleyi* and *R. simplex*, all endemic to New Zealand. The essential oil of *R. edgerleyi* and *R. simplex* consisted largely of monoterpenes. Limonene was the most abundant (23%) in *R. edgerleyi* and myrcene the most abundant (34%) in *R. simplex*. The oil of *R. simplex* lacked any significant sesquiterpenoids whereas bicyclogermacrene constituted 12% of the oil of *R. edgerleyi.* The oil of *R. anomalus* contained monoterpenes in low abundance and the sesquiterpenoids germacrene-B (15%) and γ-muurolene (16%) dominated the composition of this oil. The oil of *R. edgerleyi* had a pleasant fresh green aroma but the low yields of all three oils excluded them from potential commercial use.

Key words: Raukaua anomalus, *edgerleyi* and *simplex*, Araliaceae, Essential Oil

Introduction

A small number of plants within the New Zealand flora are known to have aromatic leaves, which afford "essential" oils upon distillation with steam (Cooper and Cambie, 1991). One such plant is *Raukaua edgerleyi* (Hook. f.) Seem. (Maori name, Raukawa). The native Maori people of New Zealand are known to have used the leaves of this plant to scent oils which were then applied to their bodies as a perfume. The earliest such record of this practice is that of the botanist Colenso (1868), who observed that "Oil for anointing was expressed from the beaten seeds of the Titoki or Titongi (*Alectryon excelsum*) and also from the seeds of the Kohia (*Passiflora tetrandra*). A gum resin, used to perfume their oil was obtained from Kohuhu and the Tarata … The aromatic leaves of the Raukawa, a very scarce small tree, sparsely growing in the high dense forests (*Panax edgerleyi*) were also sought for a similar purpose, particularly to rub their limbs and bodies." In an early publication describing the flora of New Zealand, Kirk (1889) wrote "The Raukawa is prized by the Natives on account of its perfume: Mr. Colenso states that they rub their limbs and bodies with the fresh leaves and I have been informed that the leaves are also used for scenting oil. It seems probable that the perfume might be extracted and form a profitable article of commerce." Similarly, Cheeseman (1925) noted that "The Maoris formerly mixed the fragrant leaves with fat or oil and then used the mixture for anointing the person." This paper examines the composition of the leaf essential oils of the title species, to determine whether these oils meet the expectation of Kirk, quoted above.

Materials and Methods

Plant material

Leaf material was collected in March (late summer to early autumn) from specimens, which were growing in the Otari Native Plant Reserve, Wellington, where documentation for the specimens is held.

Isolation of leaf oil

The fresh leaves (150 g) were covered with water (3.5 l), which was boiled for 4 h and the oil was isolated by hydrodistillation. The distillate was extracted with dichloromethane (3 × 25 ml). The extract was dried over magnesium sulfate and the solvent was removed on a rotary evaporator at 40 °C and atmospheric pressure.

Analysis of oil composition

Combined gas chromatography and mass spectrometry was carried out on a Hewlett-Packard (HP) 5890 gas chromatograph coupled to a HP 5970 mass selective detector, using the following conditions: column, Zebron ZB-1 (100% methylpolysiloxane), 30 m × 0.25 mm with film thickness 0.25 μm; carrier gas (He) flow rate of 70 ml/min was split 70:1; injector temperature, 250 °C; trans-

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fer line, 280 °C; temperature program, 60 °C (1 min), and then 5 °C/min to 280 °C. The solvent delay was 2 min and mass spectrometry was performed at 70 eV and 1.75 scans/s from *m/z* 41–500. The oil composition was determined from the mass spectral total ion chromatogram (TIC), which was integrated using the HP Standard ChemStation software, version A.03.00. If the chromatogram obtained by FID was significantly different from that obtained by TIC, then the differences are explained below. Only those components of the leaf oils, which exceeded 0.5% in abundance, were recorded. Leaf material was taken from only a few specimens, which may not have been truly representative of the species. Components were identified by comparison of their (Kovats) retention indices and mass spectra with those recorded by Adams (2001) and the National Bureau of Standards 75K mass spectral library.

Results and Discussion

The Araliaceae is a mainly tropical family of 65 genera, some of which occur in temperate regions. 6 of these genera are represented in New Zealand and of these, *Pseudopanax* is the most specious. The genus *Raukaua* Seem. possesses three species, *R. edgerleyi*, *R. simplex* (G. Forst.) A. D. Mitchell, D. Frodin & M. Heads, comb. nov. and *R. anomalus* (Hook.) A. D. Mitchell, D. Frodin & M. Heads, comb. nov., all endemic to New Zealand. These three species, together with other members of the New Zealand Araliaceae have undergone several taxonomic revisions over the past two centuries. They have been placed at some time in the *Neopanax*, *Nothopanax*, *Panax* and *Pseudopanax* genera. After a study of morphological characters, Philipson (1965) concluded that "no satisfactory subdivision of the New Zealand species can be made. … The proper course, therefore, is to treat all the species as belonging to a single genus," viz., *Pseudopanax.* More recently, following a study of ribosomal DNA sequences and morphological data, these three species were separated from *Pseudopanax* and placed in the reinstated genus *Raukaua* (Mitchell *et al.*, 1997).

R. edgerleyi is an attractive tree, 10–15 metres tall with an open form, which grows throughout New Zealand in lowland forest. It has prominently-veined long-petioled unifoliate lanceolate dark-green glossy leaves, about 10 cm in length, which when crushed, emit a pleasant aroma.

R. simplex (Maori name, Haumakaroa) is a small tree, about 8 metres tall, with a similar distribution to the Raukawa and which also has similar leaves except that these lack the deep-green colour and have a serrated margin.

R. anomalus is a divaricating shrub up to 3 metres tall. Like the other two species, it grows throughout New Zealand but prefers the margins of lowland forest. It has unifoliate orbicular leaves, about 1 cm in length on a very small petiole.

Previous work

The essential oil of *R. simplex* was analyzed by Murray and Stanley in 1952 before the availability of gas chromatography. They found that the yield of oil varied from 0.15% in the spring to 0.06% in the autumn. The autumn leaf oil, which was fractionated by classical vacuum distillation, was dominated by monoterpenes, including myrcene 34%, α-pinene 13% and dipentene 4%. 3% of the oil was composed of camphorenes, which are dimers of myrcene. Paraffins, which will have originated from the leaf wax, constituted 20% of the oil and sesquiterpenes less than 5%, of which aromadendrene was the only one identified. Murray and Stanley also noted that *R. edgerleyi* afforded an essential oil in 0.2% yield, which was composed mainly of terpenes including myrcene.

Very little work has been recorded on the essential oils which occur in plants within the genera *Nothopanax*, *Neopanax* and *Pseudopanax* which are closely related to *Raukaua.* Murray and Stanley briefly examined the compositions of essential oils of several New Zealand *Pseudopanax* species and recorded that *P. colensoi* afforded a mixture of solid paraffins with only traces of other constituents while the other species yielded small percentages of essential oils, the main constituents of which were paraffins and azulene sesquiterpenes. More recently, *Nothopanax delavayi* was shown to afford an essential oil in a yield of 0.4–0.6%, the major components of which were β-phellandrene (25.4%), myrcene (19.3%) and α-pinene (11.3%) (Hu *et al.*, 1991). The volatile leaf oil of *Nothopanax fruticosum* was obtained in 0.32% yield and contained only sesquiterpene hydrocarbons (Oliveros-Belardo *et al.*, 1995). The compositions of essential oils from several Araliad species, which are more distantly related to those of *Raukaua*, are summarized by Hegnauer (1989). From the published work, it appears that these species afford leaf oils which consist largely of monoterpenes but a small number of species within this family provide oils which are comprised largely of sesquiterpenes and some with only wax hydrocarbons. This paper examines the oils of the 3 species belonging to the *Raukaua* genus and a later paper will examine oils from some New Zealand *Pseudopanax* species for comparison.

Raukaua simplex and *R. edgerleyi*

Morphologically, *R. simplex* and *R. edgerleyi* are easily differentiated, but nevertheless are quite similar. This similarity is mirrored in the composition of the essential oils. Over 50% of the oils of both *R. simplex* and *R. edgerleyi* consisted of monoterpenes (Table I). However, β-myrcene comprised more than one third of the oil of *R. simplex* whereas 22.6% of the oil of *R. edgerleyi* was limo-

Table I. Composition[1] (in %) of the essential oils of the leaves of *Raukaua* species.

	Component	RT[2]	KI[3]	*R. simplex*	*R. edgerleyi*	*R. anomalus*
1	Hexanal	6.1	804	–	–	1.3
2	(*E*)-2-Hexenal	7.3	855	–	–	1.4
3	(*Z*)-3-Hexenol	7.5	861	–	–	5.5
4	Hexanol	7.9	873	–	–	2.4
5	α-Pinene	10.6	940	13.0	7.8	–
6	β-Pinene	12.1	980	0.5	2.4	–
7	β-Myrcene	12.5	992	34.0	9.3	0.6
8	Limonene	14.3	1030	4.0	22.6	–
9	Linalool	16.9	1094	–	–	2.3
10	Terpinen-4-ol	20.4	1169	–	1.6	–
11	α-Terpineol	20.9	1179	–	8.5	1.5
12	δ-Elemene	28.1	1339	–	2.1	1.6
13	β-Elemene	30.3	1390	–	0.8	1.6
14	(*E*)-Caryophyllene	31.6	1423	–	–	2.5
15	γ-Elemene	32.0	1432	–	0.9	9.2
16	Aromadendrene	32.4	1444	1.0	0.6	–
17	α-Humulene	32.9	1456	–	–	2.1
18	9-*Epi*-caryophyllene	33.2	1463	–	–	0.9
19	γ-Muurolene	33.8	1473	–	–	16.2
20	Germacrene-D	34.0	1481	–	6.5	4.9
21	Bicyclogermacrene	34.6	1499	–	11.8	8.9
22	γ-Cadinene	35.2	1512	–	–	0.6
23	δ-Cadinene	35.5	1526	–	–	1.8
24	Elemol	36.3	1538	–	0.6	–
25	Germacrene-B	36.9	1557	–	1.3	14.9
26	Spathulenol	37.5	1570	–	5.9	–
27	Globulol	37.6	1575	–	0.9	–
28	Viridiflorol	37.8	1580	–	1.8	1.4
29	Sesquiterpene alcohol[4]	38.1	1587	–	1.4	1.5
30	β-Atlantol	39.2	1616	–	1.2	–
31	*Epi*-α-cadinol	39.8	1631	–	0.6	–
32	*Epi*-α-muurolol	40.2	1643	–	1.6	1.7
33	7(11)-Eudesmen-4-ol	41.7	1685	–	–	1.8
34	Diterpenoid[4]	56.8	2257	–	1.0	–
35	Diterpenoid[4]	59.5	2328	–	0.8	–
36	Pentacosane	66.6	2500	–	–	2.7
37	Heptacosane	71.5	2698	–	0.8	9.8
Oil yield [g/kg fresh leaves]				0.6	2.3	1.4

[1] Determined by integration of the GC-MS total ion chromatogram (≥ 0.5%).
[2] In minutes.
[3] Kovats Index.
[4] See discussion.

nene, which provided the latter with a very pleasant refreshing aroma, distinguished by a hint of lemon.

In Murray and Stanley's early work, which was not repeated for this paper, sesquiterpenes were found to make up less than 10% of the oil of *R. simplex*, whereas they constituted nearly 40% of the oil of *R. edgerleyi.* Of these, the biosynthetically closely related bicyclogermacrene (11.8%), germacrene D (6.5%) and spathulenol (5.9%) were the most notably abundant. Component 29 could not be identified but it possessed a mass spectrum which suggested that it belonged to the hydroazulene alcohol group of products, but was more polar than the isomeric components 26–28. The minor diterpenoid components 34 and 35 had mass spectra resembling that of sandaracopimarinal but were more polar and might have been the isomeric pair of pimarinal and isopimarinal.

Raukaua anomalus

As its name suggests, this species is morphologically quite different from the other two species. It has considerably smaller leaves and a totally dissimilar growth habit. These variances from its fellow species are reflected in the composition of the essential oil. The oil consisted of a group of hexane derivatives and some long-chain wax hydrocarbons but more than 60% of the oil consisted of sesquiterpenoids. Of these, germacrene-B (14.9%) and γ-muurolene (16.2%) were particularly prominent in the chromatogram. It should be noted that the abundance of γ-elemene was probably false since comparison of the MS-TIC with the GC-FID showed that this component was only a minor one in the FID chromatogram and that this component had arisen during the short period between analyses by the two different methods. Germacrene-B is one of the two major components of this oil and a Cope rearrangement of this product will readily give rise directly to γ-elemene (Jones and Sutherland, 1968).

Taxonomy

It is interesting that the major sesquiterpenoids in the oil of *R. anomalus* are all derived from bicyclogermacrene and therefore are all closely related. This was also the case with the components of the other *Raukaua* oils and this close chemical relationship mirrors the close taxonomic relationship that has been constructed for these species. This relationship is to be expected since the existence of the enzymes, which control the synthesis of the sesquiterpenoids, is determined by the similar genetic constitution of the species. On the other hand, the differences in oil composition, which are seen between this and the other 2 species are also reflected in the different morphological features mentioned above, for the same reason.

Oil aroma

The oil of *R. edgerleyi* had a pleasant fresh green aroma, due to its monoterpenes and this fragrance was utilized culturally by the Maori people of New Zealand (see introduction). However, the low yield of this and the oils of the other 2 species would exclude them from potential commercial use.

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