Essential Oils from the Leaves of Three New Zealand Species of *Pseudopanax* (Araliaceae)

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Essential oils from three of the eleven endemic New Zealand species of *Pseudopanax*, *P. arboreus, P. discolor* and *P. lessonii*, were found to have a fairly uniform composition which was different from that of the oils of *Raukaua* species that were formerly classified in the *Pseudopanax* genus. Oils of the three *Pseudopanax* species all contained significant proportions of viridiflorol and a closely related unidentified hydroazulene alcohol in common. In addition, the oil of *P. arboreus* contained bicyclogermacrene, linalool and long chain hydrocarbons. The oil of *P. discolor* contained nerolidol in abundance (36.3%) together with linalool and *epi*-α-muurolol. The oil of *P. lessonii* contained a complex mixture of sesquiterpene alcohols including *epi*-α-muurolol and a mixture of long chain hydrocarbons. Nerolidol and linalool provided the oil of *P. discolor* with a pleasant floral aroma, but the yield of oil was very low (0.01%).

Key words: Pseudopanax arboreus, discolor and *lessonii*, Araliaceae, Essential Oil

Introduction

The Araliaceae is a family of 65 genera and approximately 800 species, which occur mainly in tropical regions, but some genera are found in areas of temperate climate including New Zealand, where 6 genera are represented. The *Meryta, Stilbocarpa* and *Schefflera* genera each have one species in New Zealand, *Kirkophytum* has 2 species, *Raukaua* has 3 species and *Pseudopanax* has 11 species. The taxonomy of the Araliaceae has been revised several times over the past 2 centuries and the New Zealand *Pseudopanax* species have been placed at some time in the *Neopanax, Nothopanax, Panax* and *Pseudopanax* genera (Philipson, 1965; Mitchell and Wagstaff, 1997). More recently, following a study of ribosomal DNA sequences and morphological data, three of these Araliad species were separated from *Pseudopanax* and reinstated in the genus *Raukaua* (Mitchell *et al.,* 1997). The essential oils from the leaves of these 3 species were the subject of the previous paper by this author (Weston, 2003). The 11 New Zealand species of *Pseudopanax* fall roughly into 3 groups, based on morphology. The first group includes those plants which have long narrow serrated coriaceous (leather-like) leaves, typified by *P. crassifolius, P. ferox* and *P. linearis.* The second group comprises those species which have similar but much shorter leaves. Two of the species studied in this paper, *P. lessonii* and *P. discolor*, belong to this group and were selected because their leaves, when crushed, emit a weak fragrance. The third group is characterized by its shorter wider fleshier leaves and includes *P. colensoi*, *P. laetus* and *P. arboreus*, the last of which was also included in this study. Little work has been carried out to date on essential oils from *Pseudopanax* species [see Weston (2003) for a summary of the literature], so the present work was initiated to investigate the yield and composition of the leaf essential oils from 3 New Zealand *Pseudopanax* species in order to compare the data with those from the closely related *Raukaua* species previously studied and to add to our scarce knowledge of the oils from *Pseudopanax* species.

Materials and Methods

Plant material

Leaf material was collected in March (late summer – 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

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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; transfer 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 to 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

Pseudopanax arboreus

Pseudopanax arboreus (Murray) Philipson (common name, five-finger; Maori name, Whauwhaupaku) is a tree which grows up to 8 metres. It has 5–7 foliate leaves on long (20 cm) petioles and the serrated obovate leaflets (5 cm × 15 cm) possess petiolules, 5 cm long. It grows throughout New Zealand in lowland forests.

The characteristic feature of the oil of the five-finger was the abundance of bicyclogermacrene (12.9%; Table I). This product and linalool (5.6%) were the only significant components of the non-polar half of the chromatogram of this oil. Viridiflorol (12.8%) and an unidentified hydroazulene alcohol (component 26, 10.5%) both dominated the sesquiterpenoid region of the chromatogram of this oil and in fact, these two compounds were present in the oils of all three species of *Pseudopanax* which were examined here and were particularly prominent in the oils of this species and *P. lessonii.* Component 39 was prominent in a region of the chromatogram where no other products occurred. Its identity could not be established but it appeared from mass spectral data to be a long chain aldehyde. In the polar region of the chromatogram, two compounds were particularly abundant, namely pentacosane (14.5%) and heptacosane (7.2%). With the chromatographic conditions used for this work, hydrocarbons constituted nearly 30% of the oil. Earlier work by Murray and Stanley (1952) indicated that long chain hydrocarbons were abundant components of the essential oils of *Pseudopanax* species and in the case of the New Zealand species *P. colensoi* were the only components, but it is not possible to determine whether these hydrocarbons had originated from leaf cuticular wax or essential oil glands.

Pseudopanax discolor

Pseudopanax discolor (Kirk) Harms is a shrub up to 5 metres tall with 3–5 foliate elliptic leaves on petioles ~5 cm long. The lanceolate serrated leaves are green-bronze in colour. This plant grows in lowland forests, but is found naturally only in the northern half of the north island of New Zealand. Its attractive form and foliage have made it a popular plant in home gardens.

The composition of the oil of *P. discolor* was dominated by the presence of nerolidol, which constituted more than one-third of the entire oil. The next most abundant component was linalool (7.7%) and these two components were responsible for the pleasant aroma of the oil. Other significant components, which exceeded 5% in abundance, were viridiflorol (7.5%), *epi*-α-muurolol (5.1%) and an unidentified hydroazulene alcohol (component 26, 6.5%).

Pseudopanax lessonii

Pseudopanax lessonii (DC.) K. Koch (Maori name, Houpara) is a tree up to 6 metres tall. It has 3–5 foliate leaves on long petioles (10 cm) and thick obovate serrated leaflets. It grows in coastal forests and scrub and is found naturally in the northern half of the north island of New Zealand.

Table I. Composition[a] (in %) of the essential oils of the leaves of some *Pseudopanax* species.

Component	RT [min]	KI[b]	*P. arboreus*	*P. discolor*	*P. lessonii*
1 Hexanal	6.1	804	0.5	0.8	3.5
2 Furfural	6.6	835	–	–	1.8
3 Unidentified	6.9	844	–	–	0.6
4 (*Z*)-3-Hexenol	7.5	861	–	1.5	–
5 Cyclohexanone	8.3	882	–	0.5	1.4
6 Octanal	12.4	988	0.7	0.8	1.0
7 *β*-Myrcene	12.5	992	0.7	–	–
8 (*Z*)-3-Hexenyl acetate	12.7	998	–	1.0	–
9 Unidentified	12.7	999	0.6	–	–
10 Unidentified	13.4	1019	0.6	–	0.7
11 *Cis*-(furano)linalool oxide	15.7	1085	–	0.6	–
12 Unidentified	16.7	1090	–	–	3.9
13 Terpinoline	16.7	1092	0.7	–	–
14 Linalool	16.9	1094	5.6	7.7	–
15 Unidentified	19.1	1138	–	–	0.6
16 *α*-Terpineol	20.9	1179	0.6	2.5	–
17 *δ*-Elemene	28.1	1339	0.9	–	–
18 Neryl acetate	29.2	1360	0.8	–	–
19 9-*Epi*-caryophyllene	33.2	1463	–	1.3	–
20 Bicyclogermacrene	34.6	1499	12.9	1.5	3.0
21 (*E*)-Nerolidol	37.0	1560	0.8	36.3	0.8
22 Unidentified	37.2	1565	2.2	2.2	3.9
23 Ledol	37.3	1568	0.8	0.6	1.0
24 Spathulenol	37.4	1570	1.0	0.9	–
25 Viridiflorol	37.8	1580	12.8	7.5	19.6
26 Unidentified	38.1	1587	10.5	6.5	7.0
27 Unidentified	38.1	1588	–	–	11.7
28 5-*Epi*-7-*epi*-*α*-eudesmol	38.5	1605	3.8	3.0	2.5
29 Unidentified	38.6	1607	–	–	2.7
30 Unidentified	39.2	1612	1.4	1.3	2.5
31 Unidentified	39.4	1614	–	–	2.7
32 *β*-Atlantol	39.6	1616	–	0.6	–
33 Unidentified	39.8	1630	–	–	2.8
34 *Epi*-*α*-cadinol	39.8	1631	–	3.3	–
35 Unidentified	39.9	1634	–	–	0.6
36 Unidentified	39.9	1635	–	–	2.5
37 *Epi*-*α*-muurolol	40.2	1643	–	5.1	5.8
38 Benzyl salicylate	47.0	1865	–	0.5	–
39 Long chain aldehyde	47.3	1874	3.2	–	–
40 Tricosane	61.3	2302	1.6	0.7	1.5
41 Hydrocarbon	62.6	2353	2.1	3.6	1.9
42 Hydrocarbon	62.6	2354	2.2	2.4	1.1
43 Hydrocarbon	62.7	2356	–	–	1.7
44 Tetracosane	63.8	2402	1.0	–	–
45 Unidentified	64.0	2410	0.7	–	–
46 Pentacosane	66.6	2500	14.5	0.9	1.8
47 Unidentified	69.7	2627	–	–	0.6
48 Heptacosane	71.5	2698	7.2	1.7	2.0
49 Unidentified	73.2	2768	–	–	1.5
Oil yield [g/kg fresh leaves]			0.04	0.1	0.2

[a] Determined by integration of the GC-MS total ion chromatogram (≥0.5%).
[b] Kovats Index.

Unlike the oils of the previous two species, that of *P. lessonii* contained no linalool and indeed contained no detectable monoterpenes and the weak aroma of this oil was due to the "leafy" components 1–6, all of which have "green" aromas. A feature of the composition of the oil of *P. lessonii* was the large number of components which were not identified with certainty, despite the extensive

compilation of spectra in the National Bureau of Standards 75 K mass spectral library and that of Adams (2001). This was due to the complexity of the chromatogram and the unsatisfactory resolution which resulted from the large number of components particularly in the 1500–1650 region where the sesquiterpene alcohols occur. Abundant components of this oil included viridiflorol (19.6%) and two closely related hydroazulene alcohols, which were effectively coincident in the chromatogram (total 18.7%), together with a number of other unidentified sesquiterpene alcohols. Like the oil from the previous species, that of *P. lessonii* contained a notable level of *epi*-α-muurolol (5.8%) and a range of long chain hydrocarbons.

Oil aroma

Of the three oils examined in this work, that of *P. discolor* had a strong pleasant fresh green floral aroma which will have been due largely to the presence of linalool (7.7%) that is the quintessential component of floral aromas and nerolidol (36.3%), which has a fresh floral odour resembling that of rose, lily and apple (Fenaroli, 1975) and orange flowers (Poucher, 1974). None of the three species studied here afforded an essential oil in sufficient yield that would attract commercial interest.

Taxonomy

The work of Mitchell and Wagstaff (1997) showed that the 3 species studied here have a close evolutionary relationship to one another and to the other New Zealand *Pseudopanax* species, but are well separated from the *Raukaua* species, oils of which were studied in the preceding paper. If anything, *P. arboreus* is separated to a small degree from *P. discolor* and *P. lessonii* in terms of evolution, but such a distinction is not obvious from the essential oil composition. Two compounds, viridiflorol and a closely related hydroazulene alcohol were major components of and common to the oils of all three species studied here. The chromatograms and composition of these oils displayed a degree of uniformity which was reflected in the genetic and morphological analyses of Mitchell and Wagstaff (1997), but which was different from those of the *Raukaua* species studied earlier (Weston, 2003), species which were formerly classified in the *Pseudopanax* genus. The composition of the essential oils of these species therefore was consistent with the separation of these genera.

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