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THE VOLATILE LEAF OILS OF THREE SPECIES OF *LEPTOSPERMUM*

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In continuation of our work on the essential oils of the Australian native flora, we have now investigated the volatile leaf oils of the chemically hitherto unexamined myrtaceous species *Leptospermum sphaerocarpum* Cheel and the wrongly named (Thompson, J., personal communication) (but as yet not renamed) *L. lanigerum* (Ait.) Sm. var. *macrocarpum* Maiden et Betche and *L. scoparium* J. R. et G. Forst. var. *rotundifolium* Maiden et Betche. A taxonomic revision of the genus *Leptospermum*, being carried out at the National Herbarium, Royal Botanic Gardens in Sydney, indicates close botanical affinities between all three taxa but wide divergences from *L. lanigerum* var. *lanigerum* and *L. scoparium* var. *scoparium* (Thompson, J., personal communication).

An examination of the steam-distilled oils by a combination of capillary GC–MS and IR has shown significant qualitative, as well as quantitative, similarities between the three taxa investigated and thus supports their close botanical relationship. The oils are predominantly monoterpenoid and are characterized by relatively large amounts of α-pinene, 1,8-cineole and *p*-cymene. The only sesquiterpenoids present in any quantity are the alcohols viridiflorol and the isomeric α-, β- and γ-eudesmols. Significantly, sesquiterpenes are present in minor amounts only. All GLC data are summarized in Table 1. All three oils contained traces of β-triketones which, owing to lack of material, were not investigated further.

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An earlier investigation of the volatile leaf oils of *L. lanigerum* var. *lanigerum* has shown the existence of two chemical forms [1]. The so-called 'type' oil was reported to contain (+)-α-pinene, 1,8-cineole, geraniol, geranyl acetate and cinnamate, citral, sesquiterpenic alcohols and very major proportions (60–75%) of aromadendrene and 'eudesmene' (a mixture of the isomeric α-, β- and γ-selinenes). Variety 'A' oil was characterized by the presence of myrtenol and of myrtenyl acetate in addition to (+)-α-pinene. Both chemical forms were reported to contain 'phenolic' compounds, shown later to be the β-triketones grandiflorone, leptospermone and flavesone [2].

We were unable to find any evidence of geranyl acetate, geranyl cinnamate, myrtenyl acetate and of the isomeric α-, β- and γ-selinenes in the oil of *L. lanigerum* var. *macrocarpum*. Thus we support the suggestion that it is a distinct species unrelated to *L. lanigerum* var. *lanigerum*.

EXPERIMENTAL

Collection of plant material and isolation of volatile oils. *L. lanigerum* var. *macrocarpum* and *L. sphaerocarpum* were collected near Wall's Lookout in the Blue Mountains, west of Sydney. *L. scoparium* var. *rotundifolium* was collected near Tianjara Falls west of Nowra, N.S.W. Fresh foliage and terminal branchlets (400 g) were steam-distilled with cohobation in an all-glass apparatus [3] to yield pale yellow oils (Table 2).

Identification of oil constituents. Analytical GLC was conducted on a Perkin Elmer 900 gas chromatograph using 15 m ×

Table 1. % Composition*

Peak*	Compound	*L. lanigerum* var. *macrocarpum*	*L. sphaerocarpum*	*L. scoparium* var. *rotundifolium*
1	α-Thujene	3.7	0.9	0.1
2	α-Pinene	22.5	33.9	30.8
3	un	—	0.7	0.3
4	Sabinene	0.4	—	—
5	β-Pinene	2.8	5.9	1.9
6	Myrcene	0.5	—	tr
7	α-Terpinene	0.7	0.2	0.1
8	Limonene	1.2	1.9	1.2
9	1,8-Cineole	11.9	17.4	25.4
10	γ-Terpinene	6.7	1.6	0.3
11	*p*-Cymene	7.6	10.8	2.3
12	Terpinolene	1.5	0.4	tr
13	un	tr	0.2	0.4
14	Linalool	0.3	0.3	0.4
15	Terpinen-4-ol	3.2	1.7	1.3
16	un	tr	tr	0.5

Table 1—*Continued*

Peak*	Compound	*L. lanigerum* var. *macrocarpum*	*L. sphaerocarpum*	*L. scoparium* var. *rotundifolium*
17	β-Caryophyllene	0.8	0.4	0.5
18	un	0.9	1.4	1.8
19	un	tr	0.3	0.5
20	Isoborneol	0.6	0.6	0.9
21	α-Terpineol	3.0	3.8	4.7
22	Terpenyl acetate	0.9	0.6	1.3
23	Aromadendrene	1.3	1.3	0.6
24	Alloaromadendrene	tr	0.2	1.0
25	Myrtenol	—	0.8	0.3
26	Citral	—	0.6	0.1
27	Cuminyl alcohol	—	tr	0.3
28	Geraniol	0.4	0.2	1.6
29	un	—	—	0.5
30	γ-Muurolene	tr	0.7	0.5
31	un	tr	0.6	0.8
32	un	tr	tr	0.4
33	Globulol	1.9	0.4	1.1
34	un	0.8	0.2	0.4
35	Viridflorol	2.6	1.0	2.0
36	γ-Eudesmol	6.2	1.8	2.7
37	un	0.7	0.5	0.6
38	un	0.6	0.6	0.6
39	α-Eudesmol	7.4	3.3	4.5
40	β-Eudesmol	8.7	4.6	7.1

* tr: <0.1%; un = unidentified component.
† Peaks 1–12 refer to a DC 550-coated SCOT column; peaks 13–40 refer to a FFAP-coated SCOT column.

Table 2

Species	Voucher No.*	Volume of oil (ml)	n_D^{20}	$[\alpha]_D^{22}$	d_4^{20}
L. lanigerum var. *macrocarpum*	75–251	2.5	1.4831	+20°	0.9113
L. sphaerocarpum	75–250	2.0	1.4763	+ 2°	0.9015
L. scoparium var. *rotundifolium*	72–051	1.6	1.4766	+17°	0.9091

* Museum of Applied Arts and Sciences Herbarium numbers.

0.5 mm i.d. FFAP and Silicone DC550 coated SCOT columns with He as carrier gas. Individual components were identified by their retention times and by coinjection with authentic compounds. A Hewlett Packard 3370A Integrator was used to determine % compositions. MS were determined using a Pye 104 chromatograph equipped with 100 m × 0.77 mm i.d. OV-17 WCOT stainless steel columns interfaced to an AEI MS-30 instrument via a 0.1 mm thick silicone rubber membrane separator. He at 15 ml/min was the carrier gas; individual runs were temp. programmed from 100 to 230° at 3°/min. The mass spectrometer was operatored at 70 eV with the ion source at 200°. The spectra were handled by a AEI DS30 data handling system which produced standard bar-graph presentation for direct comparison with published spectra.

Isolation of β-triketones. Solutions of essential oil (1 g) in Et_2O (10 ml) were extracted with 5% aq. $NaHCO_3$ (in order to remove any traces of carboxylic acids), then with 10% Na_2CO_3 soln. The Na_2CO_3 extracts were acidified with dil HCl and extracted with Et_2O. The residues, obtained after drying and evapn of the solvent, showed in all cases intense absorption in the region 1700–1450 cm^{-1}, characteristic of β-triketones [4]. They also gave intense red colours with alcoholic $FeCl_3$. The yields were: *L. lanigerum* var. *macrocarpum*, 1.5 mg; *L. sphaerocarpum*, 2.5 mg; *L. scoparium* var. *rotundifolium*, 2 mg.

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