Phytochemistry, Vol. 26, No. 6, pp. 1673–1686, 1987.
Printed in Great Britain.

0031–9422/87 $3.00 + 0.00

ESSENTIAL OIL CONSTITUENTS OF THE GENUS *ZIERIA**

TERENCE M. FLYNN† and IAN A. SOUTHWELL‡

Biological and Chemical Research Institute, PMB 10, Rydalmere, NSW 2116, Australia

(*Revised received* 18 *September* 1986)

Key Word Index—*Zieria*; Rutaceae; essential oils; terpenoids; aromatic ethers.

Abstract—The essential oils from some 200 samples representing most of the known *Zieria* taxa were examined. The major components were benzaldehyde, (−)-car-3-en-2-one, (−)-chrysanthenone, (−)-*cis*-chrysanthenyl acetate, *trans*-chrysanthenyl acetate, citronellal, 2,6-dimethoxy-3,4-methylenedioxystyrene, elemicin, farnesol, limonene, methyl eugenol, myristicin, naphthalene, α-pinene, safrole, 2,3,4,6-tetramethoxystyrene, 2,4,6-trimethoxystyrene and zierone.

INTRODUCTION

The genus *Zieria* (tribe Boronieae) consists of prostrate shrubs to small trees with small white or pink flowers and mostly trifoliolate leaves. All but one species, *Z. chevalieri* from New Caledonia, are endemic to eastern Australia. Only in recent years has a serious attempt been made to investigate the botany of the genus systematically [1–3].

Chemical investigations have revealed cyanogenic and essential oil components. *Z. furfuracea* [4], *Z. laevigata* [4, 5], *Z. smithii* [4, 5] and *Z. smithii* var. *macrophylla* [4] (now *Z. arborescens*) have been reported to be cyanogenic. Zierin (**1**) was isolated and characterized from *Z. laevigata* [6]. Early examination of the essential oil of *Z. smithii* by Penfold [7, 8] revealed the aromatic ethers eugenol (**2**), methyl eugenol (**3**), safrole (**4**) and elemicin (**5**), and the monoterpenes α-pinene (**6**) and linalool (**7**). He also isolated, from the same species, a $C_{10}H_{14}O$ constituent which he assigned as (−)-Δ^3-caren-5,6-epoxide (**8**) [9]. Later this component was reassigned as (−)-chrysanthenone (**9a**) [10] although some doubt about this reassignment has been expressed [11]. A further $C_{10}H_{14}O$ constituent was isolated from an aged oil sample and assigned as (+)-filifolone (**10a**) by comparison with (−)-filifolone (**10b**) from *Artemesia filifolia* [12]. Penfold also examined a form of *Z. smithii* from Tasmania which was known as *Z. macrophylla* [13] (now *Z. arborescens*), and isolated limonene (**11**) and a new ketone zierone. The structure of this sesquiterpene was eventually established as (**12**) [14–19].

No further chemical work was done on the genus until the early stages of this investigation [20–22] when (−)-car-3-en-2-one (**13**) was isolated from *Z. aspalathoides* and methoxystyrenes **14–16** were detected in *Z. arborescens* 'c' form, *Z. smithii* 'd' form and *Z. chevalieri*, respectively. We now report the remainder of the identified leaf essential oil components from all available *Zieria* taxa. The *Zieria* nomenclature used in this paper is defined by Powell and Armstrong [1] and is summarized in Table 9.

The major components of the essential oil of each sample were used to divide the genus *Zieria* into chemical groups. Consequently members of group 1 contain citronellal as the major component, group 2 benzaldehyde, group 3 aromatic ethers, group 4 car-3-en-2-one, group 5 7-oxypinenes, group 6 hydrocarbons, group 7 zierone and group 8 miscellaneous constituents. Structurally similar major components were further divided into subgroups. Group 3 then is subdivided into methyl eugenol, safrole, elemicin and methoxystyrene subgroups; group 5 into chrysanthenone and chrysanthenyl acetate subgroups; and group 6 into monoterpene and sesquiterpene subgroups.

RESULTS AND DISCUSSION

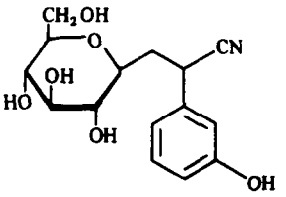
Essential oil yields from the genus *Zieria* showed wide inter- and infraspecific variation (Fig. 1). Yields ranged from 0.1% and less for *Z. involucrata* and *Z. veronicea* to 8.3 and 9.1% for *Z. smithii* sens. strict. and *Z. granulata*, respectively. Variation within the one form was as great as 0.5–8.3% for *Z. smithii* sens. strict. Some correlations between oil yield and chemistry were evident. The higher yielding specimens were generally rich in phenolic ethers or oxygenated terpenoids but those with little oil contained predominantly terpene hydrocarbons or aldehydes. With *Z. laevigata* var. *fraseri* (groups 3, 6), increased benzaldehyde content paralleled increased oil yield. The odd sample of *Z. furfuracea* sens. strict. (group 8) gave a much lower oil yield (0.1%) than the typical carenone specimens (group 4, 1.3–2.3%) and the low zierone *Z.* sp. aff. *arborescens* (group 6) gave lower oil yields (0.4%) than the typical zierone-rich specimens (group 7, 1.0–2.0%). On the other hand, the distinct chemical varieties of *Z. smithii* sens. strict. (group 3) showed no such correlation with oil yields.

The wide variation in oil yields was paralleled by the chemical variation of essential oil components. Some

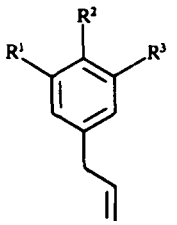
*Part 5 in the series "Phytochemistry of the Genus *Zieria*". For Part 4, see Flynn, T. M. and Southwell, I. A. (1987) *Phytochemistry* **26**,

†Present address: Standards Association of Australia, P.O. Box 458, North Sydney, NSW 2060, Australia.

‡To whom correspondence should be addressed. Present address: Agricultural Research Centre, Wollongbar, NSW 2480, Australia.

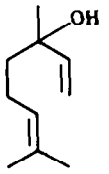


1

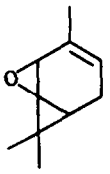


	R^1	R^2	R^3
2	H	OH	OMe
3	H	OMe	OMe
4	H	OCH_2O	
5	OMe	OMe	OMe

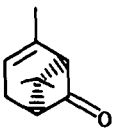
6



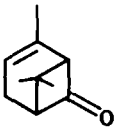
7



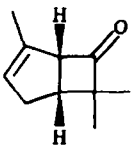
8



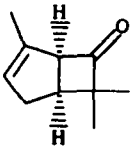
9a



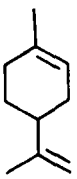
9b



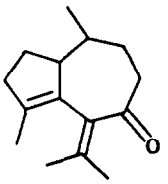
10a



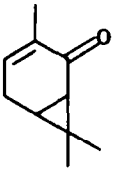
10b



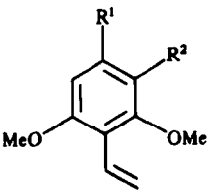
11



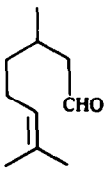
12



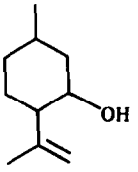
13



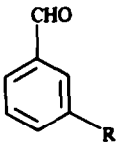
14	$R^1 = R^2 =$	OMe
15	$R^1 R^2 =$	OCH_2O
16	$R^1 =$ OMe, $R^2 =$	H



17



18



19	R =	H
21	R =	OH

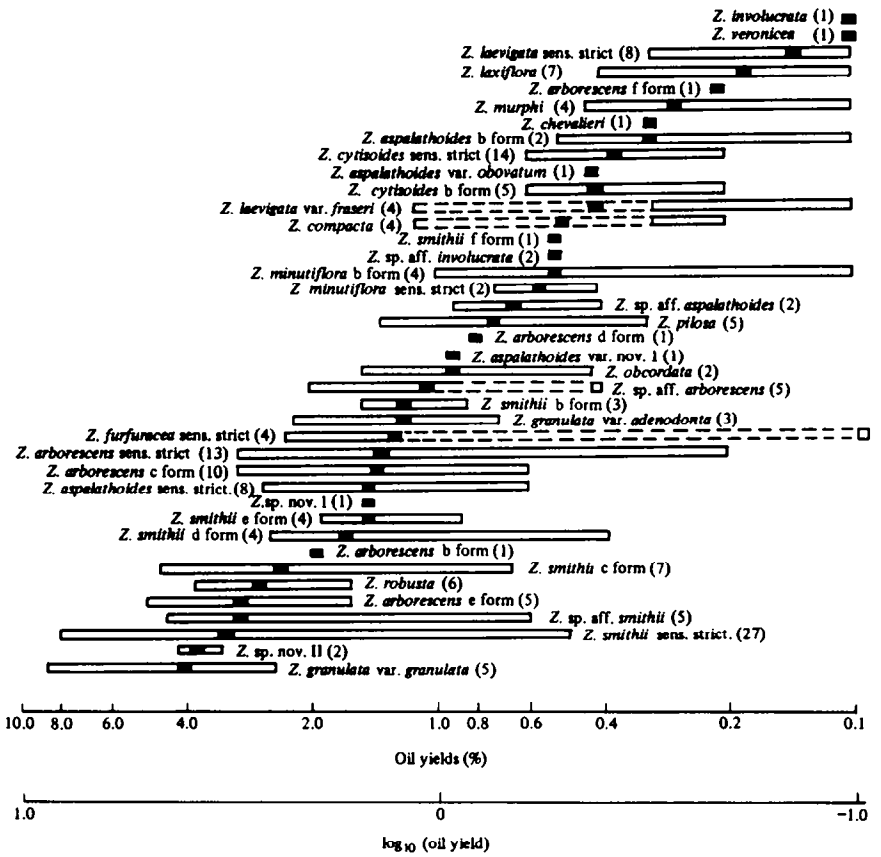


Fig. 1. Mean (solid bar) and range (open bar) percentage essential oil yield (v/w) in *Zieria* species showing the number of samples analysed (*n*) and the chemical varieties with distinctive oil yields (connected with broken bar).

species and forms are chemically variant and are represented in more than one category. The implications of this variation are the subject of a separate communication [23].

Group 1

The presence of flavouring aldehyde citronellal (**17**) was restricted to a few species only (Table 1) and even among these it was quite variable, reaching 90% at maximum levels. The predominance (90%) of citronellal (**17**) in *Z. aspalathoides* var. nov. 1 makes this species a superior source for this commercially important lemon-scented aldehyde as an oil yield of close to 1% was obtained. In comparison, *Z. veronicea* gave a poor yield (0.08%) of low-citronellal oils. The facile cyclization of this aldehyde to isopulegol (**18**) [24] accounts for the co-occurrence of this alcohol in trace (0.2–1.5%) amounts.

Group 2

Benzaldehyde (**19**) was more widespread and quantitatively more variable (Table 2) as it was detected in *Z. compacta*, *Z. laevigata* var. *fraseri* and *Z. cytisoides* sens. strict. (included in subgroup 5.2 because of substantial levels of chrysanthenyl acetate) and in minor amounts in other species. That benzaldehyde may arise as an artefact from a cyanogenic glycoside such as prunasin (**20**) [25] (Scheme 1) must be considered although hydrolysis of the known *Zieria* cyanogenic glycoside zierin (**1**) would yield *m*-hydroxybenzaldehyde (**21**). The novel styrene 2,3,4,6-tetramethoxystyrene (**14**) constituted 8% of one of the *Z. veronicea* oils but was not detected in the other.

Group 3

This aromatic ether group is made up almost entirely of taxa from the *Z. arborescens–smithii* complex. The group (Table 3) can be divided into methyl eugenol (**3**), safrole (**4**), elemicin (**5**) and styrene (**14–16**) subgroups.

Subgroup 3.1. *Z. smithii* sens. strict. gave predominantly methyl-eugenol (**3**)-rich oils (Table 3a) with significant quantities of safrole. Isolated specimens of other species (*Z. cytisoides* 'b' form, *Z. laevigata* var. *fraseri*) also gave methyl-eugenol-rich oils.

Subroup 3.2. The *Z. arborescens–smithii* complex also gave many safrole-rich oils (Table 3b) with one new species, *Z.* sp. aff. *smithii*, consistently giving 90–95% safrole (**4**).

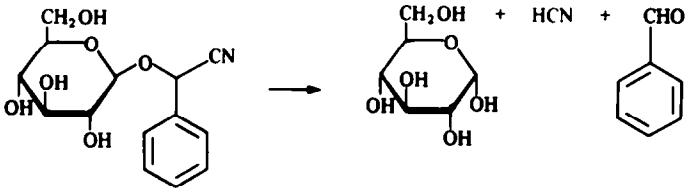
Subgroup 3.3. The *Z. arborecens–smithii* complex gave many elemicin-rich oils (Table 3c) containing up to 85% elemicin (**5**). In individual cases, where the elemicin level dropped, the aromatic ether safrole (**4**) or monoterpene hydrocarbon α-pinene (**6**) component increased. In *Z. smithii* sens. strict., the chrysanthenone (**9**) content was also significant (5–14%). Although it was from the same

Table 1. Percentages of essential oil components in *Zieria* citronellal-rich oils

RR, component	*Z. aspalathoides* var. nov. 1 ($n = 1$)	*Z. veronicea* ($n = 2$)		
		Mean	Range	s.d.
26 Limonene		17.9	2.0–33.8	22.4
56 *Citronellal*	90.0	23.7	17.8–29.5	8.3
85 Naphthalene	4.2	5.7	3.6–7.7	2.9
86 $C_{15}H_{24}$		10.4	0–20.7	14.6
88 *RR*, 88	1.0	4.7	2.1–7.2	3.6
130 $C_{15}H_{24}O$		7.6	1.0–14.1	9.3
194 2,3,4,6-Tetramethoxystyrene		4.0	0–7.9	5.6

Table 2. Percentages of essential oil components in *Zieria* benzaldehyde-rich oils

RR, component	*Z. compacta* ($n = 4$)			*Z. laevigata* var. *fraseri* ($n = 1$)
	Mean	Range	s.d.	
26 Limonene	10.3	2.8–22.0	10.3	7.0
59 Chrysanthenone	3.5	0–14.0	7.0	
60 *Benzaldehyde*	44.4	10.8–91.6	35.0	84.4
71 β-Caryophyllene	7.4	0–20.7	9.2	
79 Humulene	2.2	0–6.7	3.2	
85 Naphthalene	8.2	0–13.7	6.5	2.0
86 $C_{15}H_{24}$	1.9	0–5.4	2.6	
87 Car-3-en-2-one	3.5	0–12.4	6.0	
130 $C_{15}H_{24}O$	2.5	0–5.1	2.4	



20 Scheme 1. **19**

Table 3.(a) Percentages of essential oil components in *Zieria* aromatic ether-rich oils
(a) Subgroup 3.1: methyl-eugenol-rich oils

RR, component	*Z. cytisoides* 'b' form ($n = 1$)	*Z. laevigata* var. *fraseri* ($n = 2$)			*Z. smithii* sens. strict. ($n = 17$)		
		Mean	Range	s.d.	Mean	Range	s.d.
17 α-Pinene		9.7	0–19.4	13.7	2.8	0–9.8	3.1
55 *RR*, 55					0.9	0–5.5	1.8
59 Chrysanthenone	14.6				2.5	0–9.8	3.1
60 Benzaldehyde		5.9	0–11.8	8.3			
63 *RR*, 63					1.8	0–7.8	2.2
85 Naphthalene	2.9	9.8	9.3–10.3	0.7			
86 $C_{15}H_{24}$		4.0	0–8.0	5.7	2.3	0–7.9	2.4
87 Car-3-en-2-one	14.7						
100 Safrole		8.9	2.4–15.4	9.2	5.8	0–22.0	7.4
115 *Methyl eugenol*	53.3	24.9	15.9–33.8	12.7	73.2	42.2–93.6	14.5
130 $C_{15}H_{24}O$		9.5	4.9–14.1	6.5			
148 Elemicin					1.9	0–18.1	4.8

Table 3.(b) Subgroup 3.2: safrole-rich oils

	Z. arborescens sens. strict. ($n = 2$)			*Z. arborescens* 'c' form ($n = 3$)			*Z. smithii* sens. strict. ($n = 5$)			*Z. smithii* 'e' form ($n = 4$)			*Z. smithii* *'f' form* ($n = 1$)	*Z.* sp. aff. *smithii* ($n = 5$)		
RR$_t$ component	Mean	Range	s.d.	Mean	Range	s.d.	Mean	Range	s.d.	Mean	Range	s.d.		Mean	Range	s.d.
17 α-Pinene				5.4	1.0–14.2	7.6	7.4	0–12.3	4.6	5.2	3.3–8.3	2.2	11.0			
59 Chrysanthenone							1.8	0–5.5	2.3	19.8	10.9–27.0	6.7				
63 *RR*$_t$ 63	3.3	1.8–4.8	2.1				4.9	0–17.1	7.0							
68 *RR*$_t$ 68	5.3	4.9–5.7	0.6													
81 *RR*$_t$ 81	7.4	5.3–9.4	2.9													
85 Naphthalene	6.1	5.4–6.7	0.9	0.5	0–1.5	0.9	1.3	0–4.3	1.8	3.4	1.3–6.0	1.9	3.9	2.6	0–3.8	1.6
86 $C_{15}H_{24}$	10.7	8.7–12.6	2.8	1.0	0–3.1	1.8	0.5	0–1.3	0.7				7.4	0.4	0–1.9	0.8
87 Car-3-en-2-one	5.2	0–9.5	6.2	1.1	0–3.2	1.8	1.2	0–3.3	1.7							
100 *Safrole*	14.1	13.1–15.1	1.4	80.8	56.8–94.1	20.8	71.3	65.8–81.2	6.1	56.6	52.5–59.1	2.8	41.4	92.3	90.0–95.5	2.3
110 Zierone	5.1	3.9–6.2	1.6													
130 *RR*$_t$ 130	4.4	3.4–5.4	1.4				1.0	0–4.9	2.2				1.2			
138 Eugenol							0.3	0–1.3	0.6				27.7			
148 Elemicin				1.7	0–5.1	2.9										
176 *RR*$_t$ 176	4.1	2.6–5.6	2.1													

Table 3.(c) Subgroup 3.3: elemicin-rich oils

	Z. arborescens 'c' form ($n = 2$)			*Z. arborescens* 'e' form ($n = 5$)			*Z. smithii* sens. strict. ($n = 5$)			*Z. smithii* 'c' form ($n = 2$)			*Z. smithii* 'd' form ($n = 1$)
RR$_t$ component	Mean	Range	s.d.	Mean	Range	s.d.	Mean	Range	s.d.	Mean	Range	s.d.	
17 α-Pinene				19.0	5.0–31.1	11.0	9.1	0–15.8	6.7	6.3	2.6–9.9	5.2	
59 Chrysanthenone							8.5	0–13.8	5.9	0.8	0–1.5	1.1	
63 *RR*$_t$ 63	2.0	1.0–2.9	1.3	4.6	2.9–5.6	1.1	0.6	1.1–1.9	0.9	2.1	1.6–2.5	0.6	
67 *cis*-Chrysanthenyl acetate				7.4	3.9–12.5	3.4							
86 $C_{15}H_{24}$	5.7	3.1–8.2	3.6	1.3	0–6.4	2.9	2.5	0–5.6	2.2	2.9	1.9–3.9	1.4	3.9
100 Safrole	27.0	25.3–28.6	2.3	20.5	12.7–26.3	6.6	1.5	0–2.8	1.2	18.5	4.7–32.2	19.4	5.5
115 Methyl eugenol							1.9	0–8.1	3.5	2.0	0–3.9	2.8	
148 *Elemicin*	46.1	39.4–52.8	9.5	28.2	12.9–47.5	14.8	58.2	34.5–83.6	17.8	59.7	57.9–61.4	2.5	84.8

Table 3. (d) Subgroup 3.4: styrene oils

	Z. arborescens 'c' form						*Z. chevalieri*	*Z. smithii* 'b' form			*Z. smithii* 'd' form		
	A ($n = 2$)			B ($n = 4$)			($n = 1$)	($n = 4$)			($n = 3$)		
RR$_t$ component	Mean	Range	s.d.	Mean	Range	s.d.		Mean	Range	s.d.	Mean	Range	s.d.
17 α-Pinene	0.5	0–1.0	0.7					7.4	0–11.3	5.0			
23 Myrcene	0.6	0–1.2	0.8				20.1	8.3	1.2–19.4	7.8			
33 Terpinolene	2.8	1.2–4.4	2.3	9.8	8.5–10.7	0.9					9.8	6.9–14.2	3.9
59 Chrysanthenone								3.8	0–7.4	3.8			
63 *RR*$_t$ 63								3.0	0–6.1	3.5			
71 β-Caryophyllene	1.2	1.0–1.3	0.2	4.1	1.8–6.2	2.0	2.4	8.9	5.1–13.2	3.3	1.9	0–5.8	3.3
79 Humulene				2.5	1.3–3.4	1.1	1.8	5.2	3.5–7.7	1.8	1.1	0–3.3	1.9
82 $C_{15}H_{24}$				2.5	0–5.1	2.1	4.1				1.0	0–2.9	1.7
85 Naphthalene	6.1	3.9–8.2	3.0	4.4	2.2–5.4	1.5	10.3	3.9	3.4–5.0	0.7	2.0	0–3.0	1.7
86 $C_{15}H_{24}$	7.3	6.7–7.9	0.8	19.4	15.9–27.1	5.2		10.2	7.3–13.7	3.0	17.4	6.9–26.6	9.9
90 *RR*$_t$ 90	5.0	0–10.0	7.0	2.2	0–3.5	1.5	1.2						
100 Safrole	2.6	2.4–2.7	0.2	8.8	3.5–18.3	6.7		8.9	1.0–19.0	7.9	6.1	2.9–10.1	3.7
115 Methyl eugenol	4.7	0–9.3	6.6										
133 1,3,5-Trimethoxybenzene				1.8	1.0–2.9	0.9	18.1				2.6	1.2–4.1	1.5
194 2,3,4,6-*Tetramethoxystyrene*	56.2	53.8–58.6	3.4	3.3	1.0–5.4	1.8	3.5	22.6	10.7–42.3	13.8	7.0	2.6–9.6	3.9
205 2,4,6-*Trimethoxystyrene*				1.7	1.3–2.4	0.5	27.5				1.7	0–3.9	2.0
237 2,6-*Dimethoxy*-3,4-*methylenedioxystyrene*				18.0	16.0–21.0	2.4	1.7				27.9	6.5–41.5	18.8

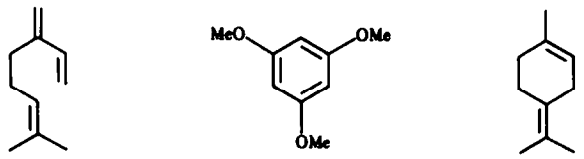
species that this novel ketone was first isolated [9, 10], higher percentages are now reported from other *Zieria* species (see Table 5a).

Subgroup 3.4. This subgroup gave oils rich in novel polymethoxylated styrenes (**14**–**16**) (Table 3d) prone to polymerization on isolation and purification [21]. *Z. smithii* 'b' form gave oils rich in 2,3,4,6-tetramethoxystyrene (**14**), *Z. smithii* 'd' form oils rich in 2,6-dimethoxy-3,4-methylenedioxystyrene (**15**) and *Z. arborescens* 'c' form oils rich in either **14** or **15**. *Z. chevalieri* from New Caledonia gave an oil rich in 2,4,6-trimethoxystyrene (**16**) with significant quantities of myrcene (**22**) and 1,3,5-trimethoxybenzene (**23**). Associated components in this group included α-pinene (**6**), myrcene (**22**), terpinolene (**24**), β-caryophyllene (**25**), humulene (**26**), an unknown $C_{15}H_{24}$ hydrocarbon and safrole (**4**). 2,4,5-Trimethoxystyrene (**27**), previously reported from *Peperomia pellucida* (Piperaceae) [26] and *Duguetia exima* [27], *Pachypodanthium staudtii* [28, 29] and *P. confine* [29] (Annonaceae), has a different methoxylation pattern to the styrenes encountered here.

Significant qualities of other aromatic ethers such as eugenol (**2**) and myristicin (**28**) have been detected in oils assigned to this and other groups (i.e. groups 3.2, 6, 7).

Group 4

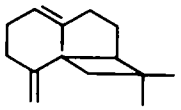
The novel ketone (−)-car-3-en-2-one (**13**), isolated first from *Z. aspalathoides* [20], characterizes this group (Table 4). *Z. granulata* var. *adenodonta* and *Z.* sp. nov. 11 gave car-3-en-2-one oils without exception whereas individual specimens of *Z. aspalathoides* sens. strict. and *Z. furfuracea* sens. strict. fall into groups 6.1 and 8, respectively. One specimen of *Z. laevigata* sens. strict. and one of *Z.* sp. aff. *involucrata* were also car-3-en-2-one-rich. The co-occurrence of significant quantities of terpinolene (**24**), car-3-ene (**29**) and eucarvone (**30**) suggest a biogenetic or chemical relationship as outlined in Scheme 2.



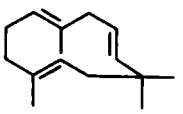
22

23

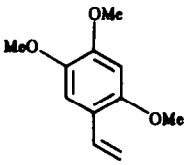
24



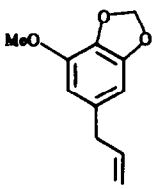
25



26



27



28

Group 5

Members of this group contain substantial amounts of 7-oxypinene derivatives chrysanthenone (**9**) or chrysanthenyl acetate (**31**, **32**).

Subgroup 5.1. The novel monoterpene ketone (−)-chrysanthenone (**9a**), isolated first from *Z. smithii* [9, 10], characterizes this group (Table 5a). *Z. aspalathoides* 'b' form, *Z. granulata*, *Z. obcordata* and *Z. robusta* gave chrysanthenone-rich oils without exception. The chrysanthenone content of one specimen of *Z. granulata* was as high as 7.2% of the whole fresh leaf weight. The quantity of this ketone present in some samples of *Z. cytisoides* 'b' form, *Z.* sp. aff. *involucrata* and *Z.* sp. nov. 1 was reduced while the alternative ketone car-3-en-2-one (**13**) and aromatic ether components increased. Chrysanthenone decomposition, consistent with previous work [12], was evident on gas chromatography at 250° block temperature but was substantially reduced at 150° block temperature. That the main decomposition product was filifolone (**10**) was evident from the work of Bates *et al.* [12] who had assigned structure **10a** to (+)-filifolone, a component isolated from aged *Z. smithii*, and the enantiomeric structure **10b** to (−)-filifolone isolated from the Arizonian sage *Artemesia filifolia*. The application of milder isolation techniques to the sage product, however, may well reveal that (+)-chrysanthenone (**9b**) is the heat and light labile precursor to (−)-filifolone (**10b**). The high yielding specimen of *Z. granulata* was subject to prolonged (24 hr) steam distillation, which extracted quantities (6% of the oil) of 3,7-dimethyl-3,6-octadienoic acid (**33**), a double-bond isomer of geranic acid. This acid was characterized (NMR, double irradiation experiments) as the methyl ester **34** which has been previously prepared by refluxing (+)-chrysanthenone (**9b**) in methanol for 16 hr [30, 31]. Thus acid **33** is probably an artefact of the prolonged distillation arising thermally as shown in Scheme 3 or photolytically as reported by Hurst and Whitham [32]. Associated compounds in this *Zieria* group include α-pinene (**6**), car-3-en-2-one (**13**), naphthalene and aromatic ethers (**3**, **4** and **14**).

Subgroup 5.2. Chrysanthenyl acetates, which characterize this group (Table 5b), have not previously been reported from the genus *Zieria*. The isolation of (−)-*cis*-chrysanthenyl acetate (**31**) from the Australian composite *Centipeda cunninghamii* in 1971 [33] was followed by the isolation of its acetate epimer, *trans*-chrysanthenyl acetate (**32**), from Japanese *Chrysanthenum* composites [34–36]. *Z. cytisoides* sens. strict. oils can be rich (approximately 50%) in either the *cis* (**31**) or *trans* (**32**) epimer, depending on location. When the ester level drops, benzaldehyde (**19**) content increases. *Z. arborescens* 'b' form and *Z. smithii* 'c' form although rich in the *cis*-epimer (**31**) contain greater proportions of associated components, especially α-pinene (**6**), a likely precursor of the chrysanthenyl acetates.

Group 6

This group contains low oil-yielding (0.001–1.2%, mean 0.34) specimens with either monoterpene or sesquiterpene hydrocarbons predominating.

Table 4. Percentages of essential oil components in *Zieria* car-3-en-2-one-rich oils

	Z. aspalathoides sens. strict. ($n = 8$)			*Z. furfuracea* sens. strict. ($n = 3$)			*Z. granulata* var. adenodonta ($n = 3$)			*Z. laevigata* sens. strict. ($n = 1$)	*Z.* sp. aff. *involucrata* ($n = 1$)	*Z.* sp. nov. 11 ($n = 2$)		
RR$_t$ component	Mean	Range	s.d.	Mean	Range	s.d.	Mean	Range	s.d.			Mean	Range	s.d.
22 Car-3-ene	12.8	7.6–21.3	5.2	7.9	5.2–12.0	3.6	9.3	8.4–10.1	0.9		3.3	5.2	4.8–5.5	0.5
33 Terpinolene	5.8	0–11.4	3.5	8.5	7.8–9.2	0.6	9.2	7.9–10.0	1.2			10.9	10.3–11.5	0.8
65 Eucarvone	1.7	0–3.4	1.0	3.1	0–7.3	3.7	1.5	0–3.4	1.6	8.5	4.2	2.8	1.9–3.7	1.3
71 Caryophyllene	2.6	0–8.4	2.5							2.5	5.6			
79 Humulene	1.5	0–3.0	1.1							2.7				
85 Naphthalene	0.8	0–2.5	1.1	0.5	0–1.4	0.8	2.1	1.0–2.9	1.0	4.9	5.7			
87 *Car-3-en-2-one*	61.3	49.5–75.3	8.6	62.4	46.8–79.4	16.3	59.5	52.6–66.6	7.0	49.1	16.7	47.2	43.4–50.9	5.3
115 Methyl eugenol				3.5	0–10.5	6.1	1.1	0–3.4	2.0	1.3	1.5	3.4	0–6.8	4.8
130 *RR*$_t$ 130											6.0			
143 *RR*$_t$ 143											6.9			
164 $C_{15}H_{22}O$							2.8	1.8-3.5	0.9			10.0	9.3–10.6	0.9

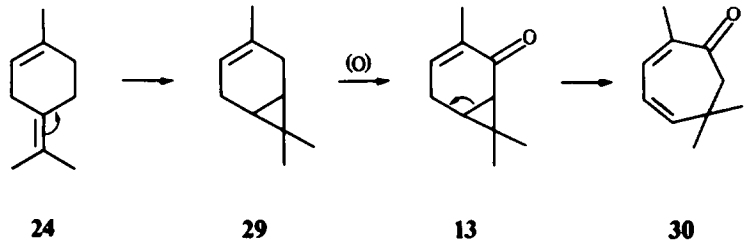
Table 5. Percentages of essential oil components in *Zieria* 7-oxypinene-rich oils

(a) Subgroup 5.1: chrysanthenone-rich oils

	Z. aspalathoides 'b' form ($n = 2$)			*Z. cytisoides* 'b' form ($n = 4$)			*Z. granulata* var. *granulata* ($n = 5$)			*Z. obcordata* ($n = 2$)			*Z. robusta* ($n = 6$)			*Z.* sp. aff. *involucrata* ($n = 1$)	*Z.* sp. nov. 1 ($n = 1$)
RR$_t$ component	Mean	Range	s.d.	Mean	Range	s.d.	Mean	Range	s.d.	Mean	Range	s.d.	Mean	Range	s.d.		
17 α-Pinene				1.5	0–2.9	1.2	4.3	1.5–7.6	2.6	3.3	2.2–4.4	1.6	7.3	4.8–9.7	2.0		
52 *RR*$_t$ 52	2.8	2.7–2.8	0.1	1.3	0–2.6	0.9	5.1	1.9–11.4	3.8	4.9	3.9–5.9	1.4	3.8	1.3–5.9	1.9		1.8
59 *Chrysanthenone*	61.3	47.2–75.3	19.9	41.0	18.2–55.2	16.2	70.0	49.9–79.4	12.6	76.4	75.7–77.1	1.0	64.2	42.8–72.8	11.2	21.3	31.3
60 Benzaldehyde				2.1	0–8.5	4.3										10.8	
75 *RR*$_t$ 75	5.3	3.4–7.2	2.7	2.3	1.9–5.2	2.2	3.8	2.6–5.3	1.0	1.2	1.1–1.2	0.1	4.4	1.6–7.6	2.2	2.8	
85 Naphthalene				6.4	3.5–9.6	3.3	0.3	0–1.7	0.8				1.2	0–3.7	1.4	5.8	12.9
87 Car-3-en-2-one	5.5	0–11.0	7.8	12.9	2.6–21.4	8.1	2.3	0–11.5	5.1	1.9	1.9	0.0	3.0	0–7.3	2.8	4.1	1.8
100 Safrole	1.4	0–2.3	1.3	4.3	1.2–11.3	4.7							0.2	0–1.0	7.0	3.5	1.0
115 Methyl eugenol				8.5	0–18.7	7.6	0.9	0–4.7	2.1	1.2	0–2.3	1.6	3.1	0–18.4	7.5	14.8	
130 *RR*$_t$ 130	10.3	1.1–19.4	12.9	1.7	0–2.6	0.9							1.8	0–4.5	1.7		2.5
168 *RR*$_t$ 168																	6.4
194 2,3,4,6-Tetra-methoxystyrene																	29.5

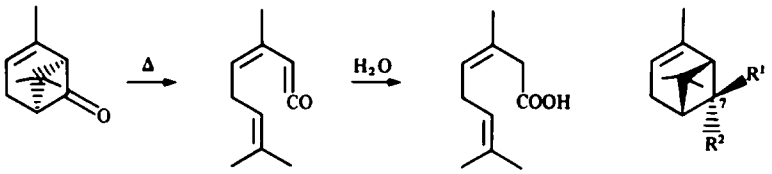
Table 5. (b) Subgroup 5.2: chrysanthenyl acetate-rich oils

	Z. arborescens 'b' form	*Z. cytisoides* sens. strict.						*Z. smithii* 'c' form		
		A			B					
	(n = 1)	(n = 3)			(n = 5)			(n = 5)		
RR, component		Mean	Range	s.d.	Mean	Range	s.d.	Mean	Range	s.d.
17 α-Pinene	14.7	16.5	4.8–22.8	10.1	4.9	0–8.2	3.6	27.3	4.7–40.7	13.9
27 β-Phellandrene		1.3	0–2.8	1.4	4.8	0–7.3	3.1			
60 Benzaldehyde		6.1	2.5–9.8	3.7	25.7	8.2–58.9	20.5			
61 trans-*Chrysanthenyl acetate*					47.6	24.3–59.7	14.1			
67 cis-*Chrysanthenyl acetate*	24.6	51.8	50.4–54.1	2.0				26.3	15.3–32.0	9.2
71 β-Caryophyllene		5.2	0–15.7	9.1						
86 $C_{15}H_{24}$	10.2									
87 $C_{10}H_{16}O$	5.9							12.7	8.0–20.5	5.0
100 Safrole	5.7									
115 Methyl eugenol	2.5							1.3	0–6.3	2.8
205 2,4,6-Trimethoxystyrene								4.2	0–12.1	5.0
237 2,6-Dimethoxy-3,4-methylenedioxystyrene								2.6	0–12.8	5.7



24 **29** **13** **30**

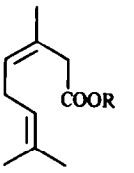
Scheme 2.



9a **33**

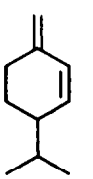
Scheme 3.

6 $R^1 = R^2 = H$
31 R^1 = OCOMe, $R^2 = H$
32 $R^1 = H$, R^2 = OCOMe

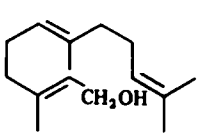


33 R = H
34 R = OMe

Subgroup 6.1. Oils from this subgroup (Table 6a) were rich in either α-pinene (**6**), limonene (**11**), β-phellandrene (**35**) or an unidentified monoterpene hydrocarbon. *Z. pilosa* oils contained, with one exception (see group 8), predominantly limonene (**11**) (58–71 %), which was also the major component of specimens of *Z. aspalathoides* sens. strict., *Z.* sp. aff. *aspalathoides*, *Z. minutiflora* sens. strict. and 'b' form. *Z. cytisoides* sens. strict. contained a chemical variant low in chrysanthenyl acetates (see group 5.2) but rich in α-pinene (**6**), which was also the major component of an individual specimen of *Z. laevigata* var. *fraseri*. β-Phellandrene (**35**) predominated in some *Z. minutiflora* 'b' form specimens and the



35



36

Table 6. Percentages of essential oil components in *Zieria* hydrocarbon-rich oils
(a) Subgroup 6.1: monoterpenes

RR, component	*Z. aspalathoides* sens. strict. ($n = 1$)	*Z. aspalathoides var. obovatum* ($n = 1$)	*Z. cytisoides* sens. strict. ($n = 5$)			*Z. laevigata* var. *fraseri* ($n = 1$)	*Z. minutiflora* sens. strict. ($n = 1$)	*Z. minutiflora* 'b' form ($n = 3$)			*Z. pilosa* ($n = 4$)			*Z.* sp. aff. *aspalathoides* ($n = 2$)		
			Mean	Range	s.d.			Mean	Range	s.d.	Mean	Range	s.d.	Mean	Range	s.d.
17 *α-Pinene*	1.8	8.0	30.6	14.4–47.5	13.5	23.4		7.0	1.0–15.8	7.8	4.2	1.5–7.4	2.5			
24 *RR*, 24		25.0				1.1		4.7	1.1–9.9	4.6				23.8	4.9–42.8	26.8
26 *Limonene*	62.3	5.6	7.8	2.5–24.8	9.5	18.2	54.0	16.1	9.8–28.7	10.9	65.3	58.1–71.3	5.4	49.1	35.5–62.6	19.2
27 *β-Phellandrene*		10.5	14.3	8.5–20.2	4.2	1.0		12.3	0–24.6	12.0				0.6	0–1.2	0.8
29 γ-Terpinene						6.1					3.5	1.2–7.3	2.7	2.4	0–4.7	3.3
57 $C_{10}H_{17}OH$								3.5	1.1–6.0	2.5						
59 Chrysanthenone			1.6	0–5.8	2.5		2.7									
60 Benzaldehyde			6.2	1.1–10.9	3.6											
67 *cis*-Chrysanthenyl acetate			1.5	0–7.3	3.3											
85 Naphthalene		4.4	8.6	3.5–15.7	6.2	11.3		2.2	0–5.0	2.5	1.2	0–2.3	1.2	0.6	0–1.2	0.8
86 $C_{15}H_{24}$		13.3	2.9	0–10.0	4.4	12.6	20.4	23.4	21.7–26.0	2.3	12.8	7.1–20.2	5.6	0.5	0–1.0	0.7
87 Car-3-en-2-one	7.2		2.5	0–12.7	5.6											
90 *RR*, 90														8.3	1.5–15.1	9.6
100 Safrole			1.3	0–2.9	1.3	6.8	2.9									
115 Methyl eugenol			3.5	0–12.3	5.4											
130 *RR*, 130	2.1		2.6	0–6.0	2.2	11.6		2.8	0–6.8	3.6						
146 *RR*, 146	6.9															
164 Farnesol								3.0	0–6.8	3.5						
189 *RR*, 189		10.7												3.4	0–6.8	4.8

Table 6. (b) Subgroup 6.2: sesquiterpenes

	Z. laevigata sens. strict. ($n = 7$)			*Z. laxiflora* ($n = 7$)			*Z. murphyi* ($n = 1$)	*Z.* sp. aff. *arborescens* ($n = 2$)		
RR, components	Mean	Range	s.d.	Mean	Range	s.d.		Mean	Range	s.d.
17 α-Pinene	4.1	0–17.8	6.3					1.1	1.1	0.0
26 Limonene	18.8	6.9–33.6	10.7	2.4	0–11.0	4.3				
58 $C_{15}H_{24}$	5.5	0–20.5	7.1	1.2	0–6.4	2.4				
60 Benzaldehyde				3.4	0–7.3	3.0				
71 β-Caryophyllene	4.4	2.1–6.8	1.5	12.7	9.5–18.6	3.2	8.9	3.6	2.3–4.9	1.8
72 *RR*, 72				2.1	0–8.1	3.3	1.1	0.8	0–1.5	1.1
79 Humulene	3.8	2.1–6.2	1.6	11.4	7.6–17.0	3.1	4.9	0.5	0–1.0	0.7
82 $C_{15}H_{24}$	1.3	0–3.0	0.9				23.6	13.3	5.6–20.9	10.8
84 $C_{15}H_{24}$	4.0	0–8.9	2.8	16.2	1.0–19.8	10.8	2.6			
85 Naphthalene	5.1	0–14.5	5.1	5.9	1.0–10.4	2.9	6.8	5.6	3.4–7.8	3.1
86 $C_{15}H_{24}$	24.3	9.6–35.5	9.6	12.6	3.5–23.7	7.0	4.3	9.3	3.7–14.8	7.8
88 *RR*, 88	0.8	0–2.0	0.9	3.2	2.1–4.1	0.8	10.4	2.1	1.1–3.1	1.4
100 Safrole				3.4	0–15.6	5.5	1.8	0.6	0–1.2	0.8
110 Zierone	0.2	0–1.4	0.5				1.8	10.1	7.6–12.6	3.5
115 Methyl eugenol							5.0	3.4	1.7–5.1	2.4
130 *RR*, 130	3.5	1.8–6.6	2.1	3.2	2.6–4.5	0.7	3.6	1.3	0–2.6	1.8
148 Elemicin				1.3	0–8.1	3.0		3.2	0–6.4	4.5
155 Myristicin	0.7	0–4.7	1.8					15.5	7.6–23.4	11.1

Table 7. Percentages of essential oil components in *Zieria* zierone-rich oils

	Z. arborescens sens. strict. ($n = 11$)			*Z. arborescens* 'd' form ($n = 1$)	*Z. arborescens* 'f' form ($n = 1$)	*Z.* sp. aff. *arborescens* ($n = 3$)		
RR, component	Mean	Range	s.d.			Mean	Range	s.d.
17 α-Pinene	2.5	0–12.1	4.0			1.3	0–1.9	1.1
27 *RR*, 27	0.5	0–5.8	1.7			0.9	0–1.4	0.8
37 *RR*, 37	0.5	0–5.3	1.6					
59 Chrysanthenone	2.2	0–16.7	5.3					
67 *cis*-Chrysanthenyl acetate	3.1	0–25.4	7.5					
71 β-Caryophyllene	0.9	0–5.4	1.8		6.1	2.7	1.8–3.3	0.8
76 *RR*, 76				23.2				
81 α-Terpineol?				11.1				
82 *RR*, 82	1.2	0–7.1	2.7			5.9	4.0–9.4	3.0
85 Naphthalene	1.4	0–6.2	2.4					
86 $C_{15}H_{24}$	7.6	2.1–21.9	5.6	17.4	6.4	4.4	3.1–6.5	1.8
87 Car-3-en-2-one	0.3	0–3.6	1.1	3.2		5.4	0–16.3	9.4
90 *RR*, 90				5.9		0.5	0–1.4	0.8
100 Safrole	1.9	0–12.3	3.8	1.0				
110 *Zierone*	44.6	16.3–67.7	20.4	14.3	10.7	43.3	42.4–45.1	1.5
115 Methyl eugenol	4.3	0–7.2	2.5	1.2		4.7	4.4–4.9	0.3
134 *RR*, 134	1.6	0–7.6	2.4					
143 *RR*, 143	2.3	0–6.9	2.5		11.8	2.2	0–3.6	1.5
155 Myristicin						6.3	1.0–16.9	9.2
237 2,6-Dimethoxy-3,4-methylenedioxystyrene	1.2	0–12.7	3.8					

unidentified $C_{10}H_{16}$ hydrocarbon in *Z. aspalathoides* var. *obovatum* and one specimen of *Z.* sp. aff. *aspalathoides*. Sesquiterpene hydrocarbons and naphthalene were also significant oil components of this group.

Subgroup 6.2. Oils rich in sesquiterpene hydrocarbons (Table 6b) included *Z. laevigata*, *Z. laxiflora*, *Z. murphyi* and a low zierone (12) variant of *Z.* sp. aff. *arborescens*.

Group 7

Zierone (**12**)-rich oils (Table 7) characterize the predominant chemical variant of *Z. arborescens* sens. strict. Zierone (**12**) was first isolated [13] and characterized [14–19] from a Tasmanian form of this species known at the time as *Z. macrophylla*. *Z.* sp. aff. *arborescens* also

Table 8. Percentage of essential oil components in *Zieria* miscellaneous oils

RR_t component	*Z. cytisoides* sens. strict. ($n = 1$)	*Z. furfuracea* sens. strict. ($n = 1$)	*Z. involucrata* ($n = 1$)	*Z. minutiflora* sens. strict. ($n = 1$)	*Z. minutiflora* 'b' form ($n = 1$)	*Z. murphyi* $n = 3$			*Z. pilosa* ($n = 1$)
						Mean	Range	s.d.	
17 α-Pinene	7.5			4.1	4.7				15.7
19 *Isobutyl butyrate*						6.6	1.6–11.2	4.8	
23 Myrcene						5.9	0–13.5	6.9	
24 RR_t 24						3.5	1.9–5.3	1.7	
26 Limonene	1.8			4.7					5.0
27 β-Phellandrene	5.5			3.7	5.2				3.4
38 *Nonan-2-one*						7.6	2.8–11.7	4.5	
53 RR_t 53						6.3	4.0–9.8	3.1	
59 Chrysanthenone			13.6						
60 Benzaldehyde	5.2								
69 *Undecan-2-one*						4.6	3.3–6.1	1.4	
71 β-Caryophyllene	6.8								
81 α-Terpineol					19.8				
82 $C_{15}H_{24}$						7.2	4.3–12.5	4.6	
83 RR_t 83						4.6	4.4–4.9	0.3	
84 $C_{15}H_{24}$						6.0	3.1–10.0	3.6	2.0
85 *Naphthalene*	23.6		35.2	4.0	7.7	5.4	3.9–6.4	1.3	2.3
86 $C_{15}H_{24}$				6.2	3.0				18.3
87 Car-3-en-2-one			10.4						
88 RR_t 88		5.4		14.1	3.8				
97 RR_t 97				35.0					
100 Safrole	22.0		10.9		4.0				
115 Methyl eugenol	4.5		3.2						5.7
130 M^+ 220	1.9	24.2	1.3		2.2				1.3
152 M^+ 216		12.3							
164 *Farnesol*					31.2				
168 M^+ 218		10.4							
218 RR_t 218									36.1

Table 9. *Zieria* nomenclature and accession numbers used in this study

Taxa sampled	Taxa as defined in ref. [1]	Accession Nos.
1. *Z. arborescens* sens. strict.	*Z. arborescens* subsp. 'a'	403, 406, 516, 517, 951, 1138, 1378, 1388, 1436, 1437, 1442, 1478, 1479
2. *Z. arborescens* 'b' form (ridged stem form)	*Z. arborescens* subsp. 'b'	398
3. *Z. arborescens* 'c' form (broad leafed form)	*Z. arborescens* subsp. 'c'	118, 862, 1374, 1449a, 1455b, 1458a, 1458b, 1459a, 1464, 1465, 1471, 1473, 1474, 1476, 1477
4. *Z. arborescens* 'd' form (glabrous form)	*Z. arborescens* subsp. 'd'	1211
5. *Z. arborescens* 'e' form (hairy stem form)	*Z. arborescens* subsp. 'e'	455, 465, 1375, 1469, 1470
6. *Z. arborescens* 'f' form (narrow leafed form)	*Z. arborescens* subsp. 'f'	1435
7. *Z. aspalathoides* sens. strict.	*Z. aspalalthoides* subsp 'a'	519, 942, 1305, 1356, 1357, 1424, 1432, 73–091, 78–075
8. *Z. aspalathoides* 'b' form (broad leafed form)	*Z. aspalathoides* subsp. 'b'	1447, 1463
9. *Z. aspalathoides* var. nov. 1	*Z.* sp. nov. 'B'	729
10. *Z. aspalathoides* var. *obovatum*	*Z.* sp. nov. 'A'	856
11. *Z. chevalieri*	*Z. chevalieri*	1296
12. *Z. compacta*	*Z. fraseri* subsp. 'b'	207, 829, 943, 943b
13. *Z. cytisoides* sens. strict.	*Z. cytisoides* subsp. 'a'	94, 522, 1111, 1113, 1301, 1431, 1431b1, 1431b2, 1431c1, 1431c2, 1431c3, 1448a, 1448b, 79–074, 79–075
14. *Z. cytisoides* 'b' form (coastal form)	*Z. cytisoides* subsp. 'b'	91, 248, 307, 399, 436
15. *Z. furfuracea* sens. strict.	*Z. furfuracea* subsp. 'a'	371, 1454, 1462c, 1462d
16. *Z. granulata* var. *granulata*	*Z. granulata*	402, 1373b, 1468
17. *Z. granulata* var. *adenodonta*	*Z.* sp. nov. C	311, 1457b, 1460
18. *Z. involucrata*	*Z. involucrata*	486
19. *Z. laevigata* sens. strict.	*Z. laevigata* subsp. 'a'	390, 525, 1428, 1430, 1440, 1444, 1445, 1484
20. *Z. laevigata* var. *fraseri*	*Z. fraseri* subsp. 'a'	1043, 1201, 1387, 1422
21. *Z. laxiflora*	*Z. laevigata* subsp. 'b'	794, 795, 797, 1404, 1405, 1419a, 1419b, 1455
22. *Z. minutiflora* sens. strict.	*Z. minutiflora* subsp. 'a'	416, 1110
23. *Z. minutiflora* 'b' form (hairy fruited form)	*Z. minutiflora* subsp. 'b'	526, 1410a, 1410b, 1482
24. *Z. murphy*	*Z. murphi*	1027, 1288, 1400, 1439, 1443
25. *Z. obcordata*	*Z. obcordata*	1302, 1354
26. *Z. pilosa*	*Z. pilosa*	906, 1109, 1401a, 1401b, 1427
27. *Z. robusta*	*Z. robusta*	167, 483, 1221, 1222, 1290, 1344, 1358
28. *Z. smithii* sens. strict.	*Z. smithii* subsp. 'a'	127, 325, 372, 400, 1081, 1084, 1085, 1189, 1203, 1385, 1389, 1402, 1403, 1416, 1420, 1425, 1429, 1446, 1449b, 1459b, 1462b, 1472, 1475, 1480, 80–049
29. *Z. smithii* 'b' form (tomentose form)	*Z. smithii* subsp. 'b'	750, 751, 753, 1411
30. *Z. smithii* 'c' form (glabrous form)	*Z. smithii* subsp. 'c'	367, 375, 1021, 1453, 1457a, 80–045, 80–046
31. *Z. smithii* 'd' form (robust mountain form)	*Z.* sp. nov. 'E' subsp. 'a'	1199, 1205, 1332, 1462
32. *Z. smithii* 'e' form (glabrous mountain form)	*Z.* sp. nov. 'E' subsp. 'b'	1406, 1407, 1408, 1409
33. *Z. smithii* 'f' form (prostrate mountain form)	*Z.* sp. nov. 'E' subsp. 'c'	1176
34. *Z.* sp. aff. *arborescens*	*Z.* sp. nov. 'F'	391, 523, 1101, 1390, 1399
35. *Z.* sp. aff. *aspalathoides*	*Z.* sp. nov. 'H'	1421, 1483
36. *Z.* sp. aff. *involucrata*	*Z.* sp. nov. 'I'	199, 908
37. *Z.* sp. aff. *smithii*	*Z.* sp. nov. 'J'	1376, 1450, 1451, 1452, 1456
38. *Z.* sp. nov. 1	*Z.* sp. nov. 'K'	1226
39. *Z.* sp. nov. 11	*Z.* sp. nov. 'G'	387, 401
40. *Z. veronicea*	*Z. veronicea*	1433, 1434

contains predominantly zierone-rich oils with *Z. arborescens* 'd' and 'f' forms yielding smaller but significant quantities of this ketone. Methyl eugenol (3) and a $C_{15}H_{24}$ sesquiterpene were the most common associated components among an almost random variety of other constituents.

Group 8

This group (Table 8) contains specimens giving oils with either a unique major component or no obvious predominant constituent. The Mt. Tomah *Z. murphyi* oils contain no component constituting more than 15% of the oil but consistently reveal isobutylbutyrate, nonan-2-one and undecan-2-one. The last mentioned ketones also occur in the genus *Ruta* [37] and the genus *Boronia* [38] also from family Rutaceae. Naphthalene is the predominant component of *Z. involucrata* and an individual specimen of *Z. cytisoides* sens. strict. Individual specimens of *Z. minutiflora* sens. strict. and 'b' form, *Z. pilosa* and *Z. furfuracea* sens. strict. contain a $C_{15}H_{24}$ sesquiterpene, farnesol (36), a high boiling unknown component and a $C_{15}H_{24}O$ major constituent, respectively.

EXPERIMENTAL

Plant material. All specimens are lodged with the National Herbarium of NSW, Sydney and voucher details are available from J. A. Armstrong, Australian National Botanic Gardens, G.P.O. Box 1777, Canberra, ACT 2601, Australia. The accession numbers of all specimens examined are given in Table 9.

Distillation procedures. Fresh, weighed leaf material was steam-distilled with cohobation and oil was collected in Hughes apparatus [39] to fractionate lighter- and heavier-than-water oils. Volatile oil yields were recorded as ml per 100 g of fresh leaf weight.

Identification of constituents. Analytical GC was conducted on a Perkin–Elmer 900 gas chromatograph using 15 m × 0.5 mm i.d. FFAP and OV17 coated stainless-steel SCOT columns with He as carrier gas. A Hewlett–Packard 3370A integrator was used to determine the percentage compositions. The tables include the percentages of all constituents > 1% where that constituent contributes 5% or greater to one or more specimens in the group. Individual components were identified by their RR_ts with respect to safrole (100) and by coinjection with authentic compounds when programmed at 6° per min to 170° after an initial time of 3 min at 80°. Except for the thermally labile chrysanthenone oils (subgroup 5.1), from one to four members of each group were subject to GC/MS analysis at 70 eV on the above stationary phases. The structures of major components were also supported by IR spectra determined as liquid films and, where necessary, by ^{1}H NMR spectra run at 100 MHz on chromatographically purified isolates in $CDCl_3$ with TMS as internal standard.

Identification of volatile acid from Z. granulata. The acid (0.06 g) from the 8–16 hr steam distillation fraction of *Z. granulata* 1468 in AR Me_2CO (4.0 ml) was stirred at 20° with freshly ignited K_2CO_3 (0.5 g) and MeI (1.0 ml). After 64 hr, filtration and concentration gave substantially pure (GC) methyl 3,7-dimethyl-3,6-octadienoate (34): IR ν_{max} cm^{-1}: 1758, 1318, 1254, 1192, 1160, 1012; ^{1}H NMR: δ ($CDCl_3$) 1.62 (3H, =CMe), 1.68 (3H, =CMe), 1.77 (3H, =CMe), 2.70 (2H, *t* (*br*), C5-H_2), 3.06 (2H, *s*, C2-H_2), 3.69 (3H, *s*, COOMe), 5.08 (1H, *t* (*br*) collapsed to *s* (*br*) on irradiation of the δ2.70 C5-H_2, =CH), 5.32 (1H, *t* (*br*) collapsed to *s* (*br*) on irradiation of δ2.70, =CH).

Acknowledgements—We thank J. A. Armstrong, Australian National Botanic Gardens, for providing most of the plant specimens and the Chemistry Departments of the New South Wales Institute of Technology, the University of Sydney and the University of New South Wales for GC/MS and NMR analyses.

REFERENCES

1. Powell, J. M. and Armstrong, J. A. (1980) *Telopea* **2**, 85.
2. Armstrong, J. A. (1987) Ph.D. Thesis. University of New South Wales. In preparation.
3. Armstrong, J. A. (1987) In preparation.
4. Smith, F. and White, C. T. (1918) *Proc. R. Soc. Queensl.* **30**, 84.
5. Petrie, J. M. (1912) *Proc. Linn. Soc. NSW* **37**, 222.
6. Finnemore, H. and Cooper, J. M. (1936) *J. Proc. R. Soc. NSW* **70**, 175.
7. Penfold, A. R. (1930) *J. Proc. R. Soc. NSW* **64**, 83.
8. Morrison, F. R., Penfold, A. R. and Simonsen, J. L. (1950) *J. Proc. R. Soc. NSW* **84**, 196.
9. Penfold, A. R., Ramage, G. R. and Simonsen, J. L. (1939) *J. Chem. Soc.* 1496.
10. Blanchard, E. P. (1958) *Chem. Ind. (London)* 293.
11. Desikan, P. (1963) *Indian J. Chem.* **1**, 186.
12. Bates, R. B., Onore, M. J., Paknikar, S. K., Steelink, C. and Blanchard, E. P. (1967) *Chem. Commun.* 1037.
13. Penfold, A. R. (1926) *J. Proc. R. Soc. NSW* **60**, 104.
14. Hildebrand, R. P. and Sutherland, M. D. (1959) *Aust. J. Chem.* **12**, 436.
15. Bradfield, A. E., Penfold, A. R. and Simonsen, J. L. (1933) *J. Proc. R. Soc. NSW* **67**, 200.
16. Birch, A. J., Collins, D. J. and Penfold, A. R. (1955) *Chem. Ind.* 1773.
17. Collins, D. J. (1959) *J. Chem. Soc.* 531.
18. Birch, A. J., Collins, D. J., Penfold, A. R. and Turnbull, J. P. (1962) *J. Chem. Soc.* 792.
19. Barton, D. H. R. and Gupta, G. S. (1962) *J. Chem. Soc.* 1961.
20. Lassak, E. V. and Southwell, I. A. (1974) *Aust. J. Chem.* **27**, 2061.
21. Southwell, I. A. (1981) *Phytochemistry* **20**, 1448.
22. Southwell, I. A. and Armstrong, J. A. (1982) *8th Int. Congr. Essent. Oils, Oct.* 1980, p. 323, Fedarom, Grasse.
23. Southwell, I. A. and Armstrong, J. A. (1987) *Phytochemistry* **26**, 1687.
24. Naves, R. (1947) *Parfums Fr.* 191.
25. Finnemore, H., Reichard, S. K. and Large, D. K. (1935) *J. Proc. R. Soc. NSW* **69**, 209.
26. Olivero-Belardo, L. (1967) *Perfum. Essent. Oil Rec.* **58**, 359.
27. Gottlieb, O. R. (1978) *Phytochemistry* **17**, 837.
28. Waterman, P. G. (1976) *Phytochemistry* **15**, 347.
29. Bevalot, F., LeBoeuf, M., Bouquet, A. and Cave, A. (1976) *Plant. Med. Phytoph.* **10**, 191.
30. Erman, W. F. (1969) *J. Am. Chem. Soc.* **91**, 779.
31. Erman, W. F., Treptow, R. S., Bakuzis, P. and Wenkert, E. (1971) *J. Am. Chem. Soc.* **93**, 657.
32. Hurst, J. J. and Whitham, G. N. (1960) *J. Chem. Soc.* 2864.
33. Pinhey, J. T. and Southwell, I. A. (1971) *Aust. J. Chem.* **24**, 1311.
34. Matsuo, A., Uchio, Y., Nakayama, M. and Hayashi, S. (1973) *Bull. Chem. Soc. Jpn.* **46**, 1565.
35. Matsuo, A., Nakayama, M., Nakamoto, T., Uchio, Y. and Hayashi, S. (1973) *Agric. Biol. Chem.* **37**, 925.
36. Uchio, Y. (1978) *Bull. Chem. Soc. Jpn.* **51**, 2342.
37. Guenther, E. (1945) in *The Essential Oils*, Vol. 2, pp. 376–377. D. Van Nostrand, New York.
38. Penfold, A. R. and Morrison, F. R. (1948) *J. Proc. R. Soc. NSW* **82**, 71.
39. Hughes, A. (1970) *Chem. Ind. (London)* **48**, 1536.