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A NEW LABDANE DERIVATIVE AND GERANYLPHLOROGLUCINOLS FROM *ACHYROCLINE ALATA**

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Key Word Index—*Achyrocline alata*; *Lucilia glomerata*; Inuleae; Compositae; *ent*-labdane derivative; phloroglucinol derivatives.

Little is known on the chemistry of the South American genus *Achyrocline* (tribe Inuleae) [1]. Only one species has been investigated so far. In addition to typical polyynes [2], some widespread terpenes, caryophyllene [3] and a flavone [4] were isolated from *A. satureioides* DC. We have now investigated a second species, *A. alata* (HBK) DC. While the roots gave no characteristic compounds, the aerial parts contain squalene, caryophyllene (**1**), copaene (**2**), 5,6-dihydroxy-3,7-dimethoxyflavone (**4**) [5] and the geranylphloroglucinols **7** and **8** [6]. In addition, two further phloroglucinols are present, both containing an additional α-pyrone ring. Structures **9** and **10** clearly follow from the ^{1}H NMR data (Table 1), which are very similar to those of known pyrone derivatives isolated from *Helichrysum* species [6–8] and to those of **7** and **8**. The two compounds, differing only in the acyl side chain, could be separated after transformation to the tetraacetates **9a** and **10a**. We have named **9** achyroclinepyrone.

Table 1. ^{1}H NMR data of **9a** and **10a** ($CDCl_3$, 270 MHz)

	9a		**10a**
7-H	3.53 *s*(*br*)		3.52 *s*(*br*)
12-H		2.56 *q*	
13-H		1.22 *t*	
14-H		1.75 *s*	
1′-H	3.09 *d*(*br*)		3.08 *d*(*br*)
2′-H		5.07 *t*(*br*)	
4′-H		2.03 *t*(*br*)	
5′-H		1.98 *dt*(*br*)	
6′-H		4.99 *t*(*br*)	
8′-H		1.58 *s*(*br*)	
9′-H		1.67 *s*(*br*)	
10′-H			
2″-H	2.92 *qq*		2.76 *tq*
3″-H	1.12 *d*		1.40 *m*
4″-H	—		0.91 *t*
5″-H	1.12 *d*		1.09 *d*
OAc	2.18 *s*		2.17 *s*
	2.19 *s*		2.19 *s*
	2.20 *s*		2.20 *s*
	2.24 *s*		2.24 *s*

J (Hz): 12, 13 = 7; 1′, 2′ = 6; 4′, 5′ = 5′, 6′ = 6.5; 2″, 3″ = 2″, 4″ = 2″, 5″ = 3″, 4″ = 7.

The polar fractions further contain a triol, which could only be isolated as its triacetate. The ^{1}H NMR data (Table 2) clearly indicate that it is the labdane derivative **6**. The stereochemistry of the 13,14-double bond follows from the chemical shifts of 14- and 16-H, which are identical to those of similar compounds [9]. The shifts of the methyl signals further indicate a *trans*-fused decalin system; while the absolute configuration is not really established, the optical rotation indicates an *ent*-labdane.

The roots of a further South American species from the tribe Inuleae, *Lucilia glomerata* Baker, only afforded humulene (**3**), while the aerial parts gave squalene.

The occurrence of **7**–**10** is interesting in so far as these compounds have only been isolated previously from *Helichrysum* species. This may indicate a close relationship

Table 2. ^{1}H NMR data of **6** (270 MHz)

	$CDCl_3$	C_6D_6
7-H	5.84 *m*	5.78 *d*(*br*)
14-H	5.56 *t*(*br*)	5.67 *t*(*br*)
15-H	4.67 *d*(*br*)	4.74 *d*(*br*)
16-H	4.63 *d*(*br*)	4.69 *d*(*br*)
16′-H	4.68 *d*(*br*)	4.75 *d*(*br*)
17-H	4.47 *d*(*br*)	4.58 *d*(*br*)
17′-H	4.57 *d*(*br*)	4.68 *d*(*br*)
18-H	0.89 *s*	0.85 *s*
19-H	0.87 *s*	0.82 *s*
20-H	0.77 *s*	0.74 *s*
OAc	2.06 *s* (6H)	1.82 *s*
	2.07 *s*	1.81 *s*
		1.72 *s*

J (Hz): 6, 7 = 5; 14, 15 = 7; 16, 16′ = 13; 17, 17′ = 12.

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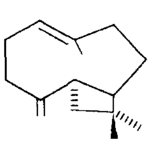
* Part 290 in the series "Naturally Occurring Terpene Derivatives". For Part 289 see Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1980) *Phytochemistry* **19**, (in press).



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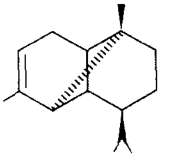

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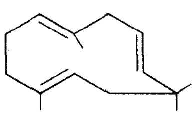

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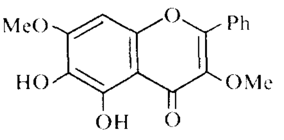

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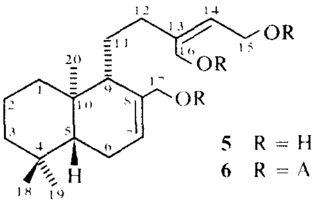
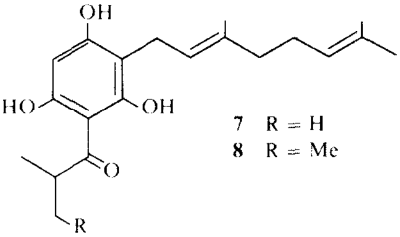
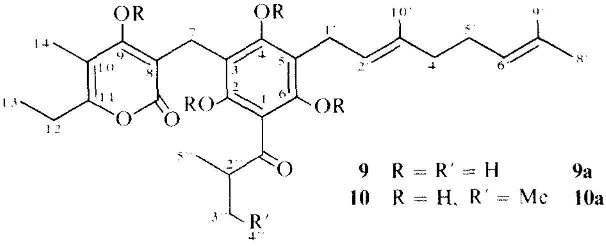


5 R = H
6 R = Ac



7 R = H
8 R = Me



9 R = R′ = H **9a** R = Ac, R′ = H
10 R = H, R′ = Me **10a** R = Ac, R′ = Me

between these two genera, while the absence of such typical constituents from the *Lucilia* species indicates it is not so closely related. However, more species need to be investigated, before these conclusions can be regarded as being definitive.

EXPERIMENTAL

^{1}H NMR: 270 MHz, TMS as internal standard; MS: 70 eV, direct inlet; optical rotation: CHCl$_3$. The air-dried plant material, collected in north-eastern Brazil, was extracted with Et$_2$O–petrol, 1:2. The extracts were separated first by column chromatography (SiO$_2$, act. grade II) and further by repeated TLC (SiO$_2$, GF 254). Known compounds were identified by comparison of the IR and ^{1}H NMR spectra with those of authentic compounds.

Achyrocline alata (*voucher RMK* 8134). The aerial parts (250 g) afforded 16 mg **1**, 22 mg **2**, 10 mg squalene, 10 mg **4**, 4 mg **5** (Et$_2$O, isolated as its triacetate **6**), 30 mg **7**, 20 mg **8**, 20 mg **9** (Et$_2$O) and 2 mg **10** (Et$_2$O, both separated as their tetraacetates **9a** and **10a**).

Lucilia glomerata (*voucher RMK* 8090). The roots (50 g) gave 2 mg **3** and the aerial parts (90 g) 3 mg squalene.

15,16,17-*Trihydroxy*-ent-*labda*-7(8),13E-*diene* (**5**). Not isolated in a pure state. Acetylation (Ac$_2$O, 1 hr, 70°) afforded the triacetate **6**, colourless gum: IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1240 (OAc), 1635 (C=C); MS *m/e* (rel. int.): M$^+$ —, 388.261 (12) (M – HOAc, C$_{24}$H$_{36}$O$_4$), 328 (23) (388 – HOAc), 268 (31) (328 – HOAc), 124 (37) (C$_9$H$_{16}^{+\cdot}$), 109 (100) (124 – $^\cdot$Me), CI (isobutane): 389 (81) (M – HOAC + 1); 329 (100) (389 – HOAc); 269 (90) (329 – HOAc).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-2.0 \quad -2.0 \quad -2.6 \quad -4.7} \ (c = 0.38).$$

Achyroclinopyrone (**9**). Only isolated as its tetraacetate **9a** (Ac$_2$O, 1 hr, 70°), colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (PhOAc), 1715 (pyrone); MS *m/e* (rel. int.): 666.304 (24) (M$^+$, C$_{37}$H$_{46}$O$_{11}$), 624 (34) (M – ketene), 582 (42) (624 – ketene), 540 (48) (582 – ketene), 497 (40) (540 – Ac$^\cdot$), 471 (35) (540 – C$_5$H$_9$), 373 (43) (540 – A$^+$), 331 (43) (373 – ketene), 167 (91) (A$^+$).

3″-*Methylachyroclinopyrone* (**10**). Only isolated as its tetraacetate **10a**, colourless gum; MS *m/e* (rel. int.): 680.327 (7%) (M$^+$, C$_{38}$H$_{48}$O$_{11}$); 638 (12) (M – ketene); 623 (4) (M – C$_4$H$_9$); 596 (13) (638 – ketene); 569 (2) (638 – C$_5$H$_9$); 553 (21) (596 – Ac$^\cdot$); 527 (6) (569 – ketene); 511 (10) (553 – ketene); 485 (11) (527 – ketene); 443 (5) (485 – ketene); 167 (33) (A$^+$); 57 (100) (C$_4$H$_9^+$).

[A$^+$ = 2-methylene-3-hydroxy-4-methyl-5-ethyl-α-pyrone ion.]

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