

LABDANE AND EUDESMANE DERIVATIVES FROM *AGERATUM FASTIGIATUM**

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Abstract—Several diterpenes, triterpenes, *ent*-labdanes and eudesmane derivatives have been isolated from *Ageratum fastigiatum*. A previously unknown eudesmane ester was characterized by its ¹H NMR spectrum as 6*α*-angeloyloxy-eudesm-4(15)-ene.

From the large genus *Ageratum* (tribe Eupatorieae, Compositae), which is placed in the Piqueria group [1], only two species have been studied chemically. So far widespread chromenes and euparin derivatives [2,3], triterpenes and flavones [3] as well as a dimer of a chromene [4] have been reported. We have now studied the constituents of *A. fastigiatum* (Gardn.) K. et R.

The roots afforded germacrene D and the dehydronerolidol derivatives **1** [5], **2** [6], **3** [7] and **4** [8].

The aerial parts gave squalene, dammadienyl acetate, taraxasteryl acetate, lupeol and its Δ⁹⁽¹¹⁾ and Δ¹²-isomers, glutinol, the eudesmane derivative **5** [9] as well as the previously unknown angelate **6**. Its structure followed from the ¹H NMR data, which were very similar to those of **5** and the known tiglate [9] (see Experimental). Furthermore some diterpenes were isolated, the *secokaurane* derivative **9** [10] and the two pairs of epimeric labdane derivatives **7a**, **7b** and **8a**, **8b** [11].

The lactols **7a** and **7b** were acetylated, but the resulting acetates **7c** and **7d** could not be separated. The structure followed from the ¹H NMR data, which were very close to those of **8a** and **8b** [11]. The position of the oxygen functions were deduced from the observed shifts of the H-16 signals in the spectra of the acetates **7c** and **7d** when compared with those of **7a** and **7b**. The absolute configuration, however, was not certain, but an *ent*-labdane was more likely, as the optical rotation was similar to that of **8a** and **8b** [11].

The chemotaxonomic situation of the genus *Ageratum* still needs further clarification by investigation of more species.

EXPERIMENTAL

The air-dried plant material (voucher RMK 8363) was extracted with Et₂O–petrol (1:2) and the resulting extracts were separated by CC (Si gel) and TLC (Si gel). The roots (205 g) afforded 60 mg germacrene D, 10 mg **1**, 20 mg **2**, 60 mg **3** and

40 mg **4**, while aerial parts (250 g) gave 5 mg squalene, 5 mg dammadienyl acetate, 15 mg taraxasteryl acetate, 20 mg lupeol together with the Δ⁹⁽¹¹⁾ and Δ¹² isomers, 25 mg glutinol, 10 mg **5**, 15 mg **6** (Et₂O–petrol, 1:10), 13 mg **7a** and **7b** (Et₂O–petrol, 1:1), 15 mg **8a** and **8b** and 6 mg **9**.

6*α*-Angeloyloxy-eudesm-4(15)-ene (**6**). Colourless oil. IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹: 1715, 1655 (C=CCO₂R); MS m/z (rel. int.): 304.240 (M⁺, 3) (C₂₀H₃₂O₂), 204 (M – Ang OH, 81), 161 (240 – C₃H₇, 100), 83 (C₄H₇CO⁺, 45), 55 (83 – CO, 54), [α]_D – 20.8° (*c* = 0.7, CHCl₃); ¹H NMR (CDCl₃): 2.28 (H-3, *brd*, *J* = 12 Hz), 1.95 (H-3', *m*), 2.08 (H-5, *brd*, *J* = 11 Hz), 5.15 (6-H, *dd*, *J* = 11, 10 Hz), 1.95 (H-11, *m*), 0.93 and 0.91 (H-12, 13, *d*, *J* = 7 Hz), 0.79 (H-14, *s*), 4.76 (H-15, *brs*) and 4.54 (H-15, *brs*), 5.93 *qq*, 1.90 *dq* and 1.83 *dq* (OAng; *J*_{3,4} ≈ 7 Hz; *J*_{3,5} = *J*_{4,5} = 1.5 Hz).

15,16-Dihydroxy-*ent*-labda-7,13-diene-15-*oic* acid lactone (**7a** and **7b**). Colourless gum, IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹: 3380 (OH), 1750 (lactone); (¹H NMR see Table 1), which were purified as their acetates **7c** and **7d**, colourless gum, which could not be separated. IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹: 3600 (OH), 1800 (γ-lactone), 1650 (C=C); MS; m/z (rel. int.) 360.230 (M⁺, 2), 300 (M – AcOH, 8), 285 (300 – Me, 5), 109 (100).

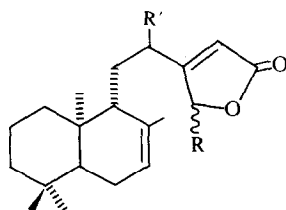
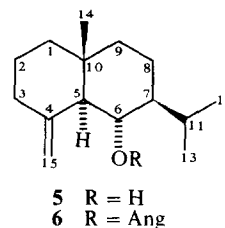
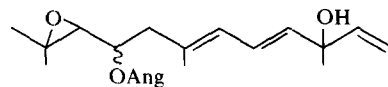
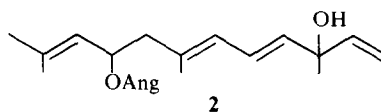
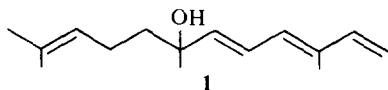
$$[\alpha]_{24}^D = \frac{589}{+7} \frac{578}{+8} \frac{546}{+9} \frac{436}{+16} \frac{365\text{nm}}{+29} \quad (c = 0.5, \text{CHCl}_3)$$

Table 1. ¹H NMR spectral data of compounds **7a–7d** (270 MHz, CDCl₃, TMS as internal standard)

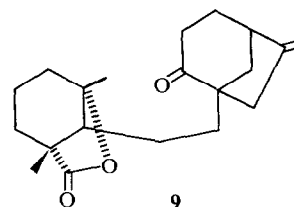
	7a	7b	7c	7d
H-8		5.46 <i>m</i>		5.46 <i>m</i>
H-12		2.53 <i>m</i>		2.58 <i>m</i>
H-12'		2.35 <i>m</i>		2.37 <i>m</i>
H-14		2.89 <i>brs</i>		5.98 <i>dd</i>
H-16		6.02 <i>brs</i>		6.86 <i>brd</i>
H-17		1.71 <i>brs</i>		1.68 <i>brs</i>
H-18		0.89 <i>s</i>		0.89
H-19		0.87 <i>s</i>		0.87
H-20	0.79 <i>s</i>	0.78 <i>s</i>	0.785	0.78
OAc	–		2.185	2.18

J: 12, 14 = 14, 16 = 1.5 Hz.

*Part 341 in the series "Naturally Occurring Terpene Derivatives". For Part 340 see Bohlmann, F., Ahmed, M., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 1439.



7a	7b	7c	7d	8a	8b
R α OH	β OH	α OAc	B-OAc	α -OH	β -OH
R' H	H	H	H	OH	OH



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