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A GERMACRANOLIDE AND A LONGIPINENE DERIVATIVE FROM *EUPATORIADELPHUS PURPUREUS**

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Key Word Index—*Eupatoriadelphus purpureus*; Compositae; sesquiterpene lactone; germacranolide; longipinene derivative; *p*-hydroxyacetophenone derivatives.

Abstract—The roots of *Eupatoriadelphus purpureus* contain tridecapentaynene, *β*-pinene and five *p*-hydroxyacetophenone derivatives. By contrast, the aerial parts have germacrene D, lupeol and its isomers, coumarin, a new sesquiterpene tiglate and a new germacranolide.

From the small genus *Eupatoriadelphus* (Compositae, tribe Eupatorieae) [1] so far only one species has been studied chemically in detail [2]. The constituents isolated showed a close relationship to the genus *Eupatorium*. Both genera were placed in the Eupatoriinae group [3]. We have now investigated a further species, *E. purpureus* (L.) K. et R. The roots afforded tridecapentaynene, *β*-pinene and the *p*-hydroxyacetophenone derivatives **2** [4], whose presence was reported earlier [5], **3** [6], **4** [7], **5** [2] and **6** [8]. The aerial parts gave germacrene D, lupeol and its isomers, coumarin, the tiglate **1** and the germacranolide **7**. The structure of **1** was deduced readily by comparing the ^{1}H NMR data (see Experimental) with those of the known angelate [7], while the ^{1}H NMR data of **7** were very close to those of other 8*β*-acyloxycostunolides [9, 10]. Though the couplings $J_{7,8}$ and $J_{8,9'}$ could not be clearly observed as the H-8 signal was a broadened doublet, the stereochemistry at C-8 was clear, as in 8*α*-acyloxy compounds large couplings are always observed. The nature of the ester residue clearly followed from the ^{1}H NMR data (Table 1). As the H-3′ signal was a quartet, the angelate had to be placed at C-5′. The compounds now isolated indicate, once more, a close relationship between *Eupatoriadelphus* and *Eupatorium*, especially since a germacranolide with a 8*β*-acyloxy group was isolated, while *p*-hydroxyacetophenones, also present in *Eupatorium* species, are particularly widespread. The chemistry of the other genera in the Eupatoriinae group is not so similar to that of *Eupatorium*.

EXPERIMENTAL

The fresh plant material (voucher 79/1493, Botanical Garden Berlin–Dahlem) was extracted with Et_2O–petrol, 1:2 and the extracts obtained were separated first by column chromatography (Si gel) and further by TLC (Si gel). Known compounds were identified by comparing their IR and ^{1}H NMR spectra with those of authentic compounds. The roots (650 g) afforded 20 mg *β*-pinene, 1 mg tridecapentaynene, 100 mg **2**, 30 mg **3**, 50 mg **4**, 100 mg **5** and 25 mg **6**, while the aerial parts (500 g) gave 40 mg germacrene D, 100 mg lupeol and its Δ9,11 and 12,13-isomers (*ca* 2:1:1), 30 mg coumarin, 20 mg **1** (Et_2O–petrol, 1:3) and 30 mg **7** (Et_2O–petrol, 3:1).

*7β-Tiglinoyloxy-*1*-oxo-α-longipinene* (**1**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1710, 1650 (C=CCO$_2$R), 1680, 1620 (C=CC=O); MS *m/z* (rel. int.): 316.204 (M^+, 1) ($C_{20}H_{28}O_3$), 233 (M − ·COR, 11), 216 (M − RCO_2H, 5), 83 ($C_4H_7CO^+$, 100), 55 (83 − CO, 72); ^{1}H NMR ($CDCl_3$): 5.79 (*dq*, *J* = 1, 1 Hz, H-2), 2.72 (*br d*, *J* = 6 Hz, H-4), 2.22 (*br s*, H-5), 4.77 (*br d*, *J* = 10 Hz, H-7), 2.84 (*br d*, *J* = 6 Hz, H-11), 1.08 (*s*, H-12), 1.01 (*s*, H-13), 0.94 (*s*, H-14), 2.06 (*d*, *J* = 1.5 Hz, H-15); OTigl: 6.87 *qq*, 1.84 *br d*, 1.88 *br s*.

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+24 \quad +26 \quad +31 \quad +75} (c = 0.4,\ \text{CHCl}_3).$$

[5′-*Angeloyloxytiglinoyloxy*]-*costunolide* (**7**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (*γ*-lactone), 1720, 1650 (C=CCO$_2$R); MS

Table 1. ^{1}H NMR spectral data of germacranolide 7 (270 MHz, $CDCl_3$, TMS as internal standard)

H-1	4.90 *br dd*	H-3′	7.14 *q*
H-2	2.4–2.0 *m*	H-4′	2.00 *d*
H-3		H-5′$_1$	4.95 *d*
H-5	4.77 *br d*	H-5′$_2$	4.86 *d*
H-6	5.12 *dd*	H-3″	6.09 *qq*
H-7	2.93 *br ddd*	H-4″	1.94 *dq*
H-8	5.85 *br d*	H-5″	1.83 *dq*
H-9	2.87 *br dd*		
H-9′	2.35 *br d*		
H-13	6.26 *d*		
H-13′	5.58 *d*		
H-14	1.48 *br s*		
H-15	1.78 *d*		

J (Hz): 1,2 = 10; 1,2′ = 7; 5,6 = 6,7 = 10; 5,15 = 1; 7,8 ~ 1; 8,9 = 4.5; 9,9′ = 15; 3′,4′ = 3″,4″ = 7; 3″,5″ = 4″,5″ = 1.5; 5′$_1$,5′$_2$ = 11.5.

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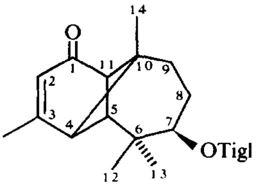
*Part 349 in the series "Naturally Occurring Terpene Derivatives". For Part 348 see Bohlmann, F., Jakupovic, J. and Schuster, A. (1981) *Phytochemistry* **20**, 1891.



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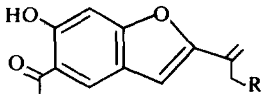
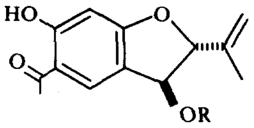
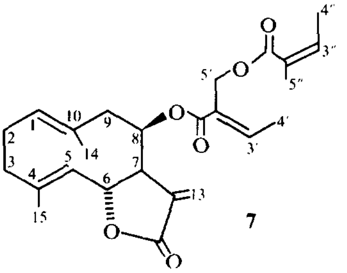


2 R = H
3 R = OH
4 R = OAc



5 R = Ang
6 R = Tigl



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m/z (rel. int.): 428 (M^+, 0.1), 329 (M − $^{\cdot}O_2CR$, 0.4), 230.131 (M − RCO_2H, 11) ($C_{15}H_{18}O_2$), 215 (230 − $^{\cdot}Me$, 4), 83 ($C_4H_7CO^+$, 100), 55 (83 − CO, 69).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+33 \quad +36 \quad +42 \quad +42}\,(c = 0.9, \text{CHCl}_3).$$

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