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SESQUITERPENE LACTONES FROM *PICRIS ECHIOIDES**

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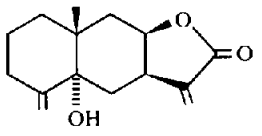
Key Word Index—*Picris echioides*; Compositae; Lactuceae; sesquiterpene lactones; germacranolide; guaianolide.

So far only little is known on the chemistry of the large genus *Picris* (Compositae, tribe Lactuceae). Flavones were isolated from two species [1] and from another sitosterol was obtained [2]. We have now investigated a further species to determine if the chemistry shows relationships to other genera of this tribe.

The aerial parts of *Picris echioides* L. afforded lupeyl acetate, lupeol, its Δ^{12}-isomer, telekin (**1**) [3], 8-deoxylactucin (**4**) [4], jaquilenin (**8**) [5] and two further lactones, **2**, the 11β,13-dihydro derivative of hanphyllin [6], and **6**, the 11-epimer of jaquilenin. However, compounds **2**, **4**, **6** and **8** could only be separated as their acetates **3**, **5**, **7** and **9** respectively. The structures of **3** and **7** could be deduced from their ^{1}H NMR spectral data (Table 1). Irradiation of the signal of the triplet at δ 4.56 led to the assignment of the signals for H-5 and H-7, while further spin decoupling starting with the double doublet at 5.16 allowed the assignment of the signals for H-1 and H-2. Irradiation of the methyl doublet collapsed the double quartet at 2.25 to a doublet. The observed coupling $J_{7,11}$ and the chemical shift of H-13 led to the assignment of the stereochemistry at C-11, especially if the values were compared with those of similar C-11 epimers. The 3β-orientation of the oxygen function followed from the couplings observed, which were in agreement with those of similar 3β-oxygenated germacranolides. The ^{1}H NMR spectral data of **7** (Table 1) were close to those of **5** and **9**. The chemical shift of H-13 and the coupling $J_{7,11}$ indicated an 11β-methyl group.

The results obtained for this *Picris* species showed that lactucin-like sesquiterpenes may be characteristic at least for some groups of the Lactuceae. Furthermore, the



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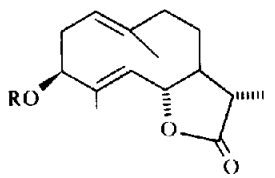

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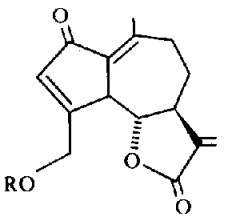
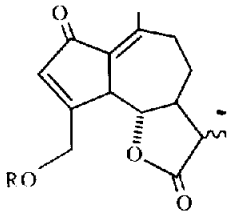
3 R = Ac



4 R = H
5 R = Ac



6 R = H, 11αH
7 R = Ac, 11αH
8 R = H, 11βH
9 R = Ac, 11βH

*Part 361 in the series "Naturally Occurring Terpene Derivatives". For Part 360 see Bohlmann, F., Adler, A., Schuster, A., Gupta, R. K., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 1899.

Table 1. ^{1}H NMR spectral data of compounds **3** and **7** (400 MHz, $CDCl_3$, TMS as internal standard)

	3	**7**
H-1	4.88 *dd* (*br*)	—
H-2	2.51 *ddd*	—
H-2′	2.30 *ddd*	—
H-3	5.16 *dd*	6.31 *dt*
H-5	4.78 *d*(*br*)	3.58 *d*(*br*)
H-6	4.56 *dd*	3.81 *dd*
H-7	1.63 *m*	2.00 *m*
H-8	1.88 *dd* (*br*)	1.87 *m*
H-8′	1.63 *m*	
H-9	2.37 *m*	2.45 *m*
H-9′	2.03 *dd* (*br*)	2.35 *m*
H-11	2.25 *dq*	2.27 *dq*
H-13	1.25 *d*	1.13 *d*
H-14	1.45 *s* (*br*)	2.44 *s* (*br*)
H-15	1.69 *d*	5.21 *dd* 4.97 *d* (*br*)
OAc	2.10 *s*	2.13 *s*

J(Hz): Compound **3**: 1,2 = 4; 1,2′ = 11; 2,3 = 5.5; 2′,3 = 10; 2,2′ = 12; 5,6 = 10; 6,7 = 8.5; 7.8 = 6; 7,11 = 11; 8,8′ = 13; 8,9 = 10; 9,9′ = 13.5; 11,13 = 7; compound **7**: 3,5 = 3,15 = 1.3; 5,6 = 6,7 = 10; 7,11 = 7; 11,13 = 7.5.

presence of 11,13-dihydro compounds seems to be typical. However, the concentrations are very low and therefore the presence of these compounds may have been overlooked in several cases. Similar results were obtained from other genera which are related to *Picris* [7–10], though only a small number of plants of the Lactuceae have been studied so far.

EXPERIMENTAL

The air-dried aerial parts (200 g) (voucher RMK 8408) were extracted with Et_2O–petrol (1:2) and the resulting extract was first separated by CC on Si gel and further by repeated TLC on Si gel. The polar fractions could not be separated by HPLC (reversed phase, MeOH–H_2O, 3:2). Acetylation (Ac_2O, 2 hr, 70°) gave the acetates, which were separated by TLC (C_6H_6–CH_2Cl_2–Et_2O, 2:2:1, several times). Finally 20 mg lupeyl acetate, 30 mg lupeol, 10 mg of its Δ^{12}-isomer, 2 mg **1**, 0.5 mg **3**, 8 mg **5**, 1 mg **7** and 1 mg **9** were obtained. The known compounds were identified by their ^{1}H NMR spectra, which were in agreement with those in the literature.

3β-Acetoxy-11β,13-dihydrocostunolide (**3**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (γ-lactone), 1740, 1240 (OAc); MS *m/z* (rel. int.): 292.167 [M]$^+$ (14) ($C_{17}H_{24}O_4$), 250 [M − ketene]$^+$ (100), 232 [M − HOAc]$^+$ (55), 217 [232 − Me]$^+$ (14); $[\alpha]_D \sim +100°$ (*c* = 0.03, $CHCl_3$).

11-Epi-*jaquilenin acetate* (**7**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1790 (γ-lactone), 1750, 1225 (OAc), 1690, 1620 (C=CC=O); MS *m/z* (rel. int.): 304.137 [M]$^+$ (3) ($C_{17}H_{20}O_5$), 262 [M − ketene]$^+$ (21), 244 [M − HOAc]$^+$ (100), 229 [244 − Me]$^+$ (3), 216 [244 − CO]$^+$ (10), 201 [216 − Me]$^+$ (10), 188 [216 − CO]$^+$ (39); $[\alpha]_D \sim +40°$ (*c* = 0.1, $CHCl_3$).

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