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THREE GUAIANOLIDES FROM *HYPOCHOERIS RADICATA**

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Key Word Index—*Hypochoeris radicata*; Compositae; new guaianolides; sesquiterpene lactones.

So far little is known about the chemistry of the genus *Hypochoeris* (tribe Cichorieae). Flavonoids are known from three species [1], while in one species several guaianolides and an eudesmanolide are present [2]. We have now re-investigated *Hypochoeris radicata* L.; so far only the presence of the flavones luteolin and isoetin has been reported [1].

The roots of *H. radicata* L. afforded a mixture of triterpene acetates, only the lupeol derivative **1** being identified. The more polar fractions contain a complex mixture of sesquiterpene lactones, which could only be partly separated. Intensive ^{1}H NMR studies led to the structures **2**, **4** and **5**. The presence of a cinnamic ester in **2** and a methacrylate in **4** and **5** easily could be deduced from the NMR data (see Table 1). Irradiation of the doublet at δ 6.42 sharpens the broadened doublets of 14-H and in the ^{1}H NMR spectrum of the corresponding acetate **3** the 3-H signal is shifted to higher fields. On irradiation at 4.42 the doublet of doublets at 3.34 collapses to a doublet and the four-fold doublet at 3.21 to a broadened doublet. Irradiation of the latter collapses the 13-H doublets to singlets and the three-fold doublet at 5.32 to a doublet of doublets, clearly indicating that the signal at 3.21 must be assigned to 7-H and consequently the signals for 5-H, 6-H and 8-H can be assigned too. The observed couplings of 8-H and those of 6-H indicate the stereochemistry at C-5 to C-8. The configuration at C-10 only can be assigned indirectly. In the NMR spectrum of **2** the signal of 1-H could be assigned. Inspection of models shows that the observed couplings are in better agreement with a β-orientation of the 10-methyl group, since the *cis*-annelation of the rings clearly follows from the coupling $J_{1,5}$. The ^{1}H NMR spectrum of **4** (see Table 1) clearly shows that only the ester group is changed, as all signals are nearly identical with those of **2**. Though **5** could not be separated from **4**, the NMR data indicate that it is the 11,13-dihydro derivative of **4**. The stereochemistry at C-11, however, could not be assigned as the signal of 11-H is overlapped by other multiplets. We have named the desacyl derivative of **2** and **4** hyporadiolide. The aerial parts contain, in addition to **1**, **2**, **4** and **5**, the ester **6**. This investigation shows that guaianolides may be characteristic for the genus *Hypochoeris*.

EXPERIMENTAL

The fresh plant material (grown from seeds Botanical Garden Köln, voucher 79/1387) was cut and extracted with Et_2O–petrol (1:2). The resulting extracts were first separated by CC (Si gel, act. grade II) and further by repeated TLC (Si gel, GF 254). Roots (220 g) afforded 30 mg **1**, 15 mg **2** (Et_2O), 7 mg **4** (Et_2O) and 7 mg **5** (Et_2O) and aerial parts (2.15 kg) 30 mg **1**, 10 mg **2**, 5 mg **4**, 5 mg **5** and 20 mg **6**.

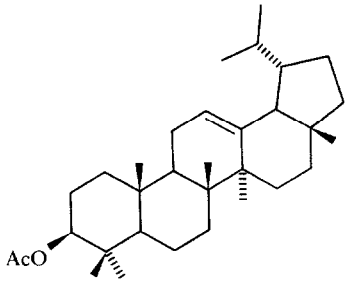
Hyporadiolide-8-O-*cinnamate* (**2**). Colourless gum, IR (CCl_4) cm^{-1}: 3620 (OH), 1780 (lactone), 1715, 1645 (C=CCO_2R, C=CCO); MS (CI, isobutane): 409 ($C_{24}H_{24}O_6$) ($M^+ + 1$, 5%); 391 ($M - H_2O$, 8); 261 (PhCH=$CHCO_2H$, 97); 149

* Part 280 in the series "Naturally Occurring Terpene Derivatives". For Part 279 see: Bohlmann, F., Rosenberg, E., Robinson, H. and King, R. M. (1980) *Phytochemistry* **19**, 2047

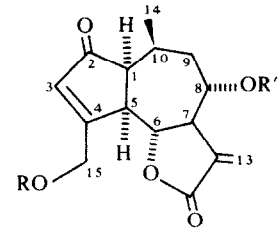
Table 1. ^{1}H NMR data of **2**–**5** (270 MHz, $CDCl_3$, TMS as internal standard)

	2	3	4	5
1-H	2.85 *m*	2.86 *dd*	2.83 *m*	2.83 *m*
3-H	6.42 *t*	6.23 *t*	6.42 *t*	6.42 *t*
5-H	3.34 *dd(br)*	3.34 *dd(br)*	3.32 *dd(br)*	3.32 *dd(br)*
6-H	4.42 *dd*	4.43 *dd*	4.40 *dd*	4.46 *dd*
7-H	3.21 *dddd*	3.21 *dddd*	3.22 *dddd*	2.60 *m*
8-H	5.32 *ddd*	5.32 *ddd*	5.25 *ddd*	5.25 *ddd*
10-H	2.68 *m*	2.65 *m*	2.67 *m*	2.67 *m*
13-H	6.34 *d*	6.34 *d*	6.33 *d*	1.33 *d*
13′-H	5.89 *d*	5.87 *d*	5.82 *d*	
14-H	4.62 *d(br)*	5.03 *d(br)*	4.62 *d(br)*	4.62 *d(br)*
14′-H	4.80 *d(br)*	5.22 *d(br)*	4.80 *d(br)*	4.80 *d(br)*
15-H	1.02 *d*	1.03 *d*	1.00 *d*	0.92 *d*
OCOR	6.47 *d*		6.17 *s(br)*	6.14 *s(br)*
	7.76 *d*		5.71 *s(br)*	5.67 *s(br)*
	7.43 *m* (3H)		1.99 *s(br)*	1.97 *s(br)*
	7.56 *m* (2H)			
OAc	—	2.06 *s*	—	—

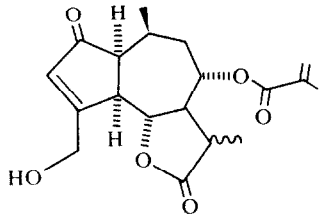
J (Hz): 1,5 = 6; 1,10 = 9; 3,14 = 1.5; 5,6 = 6,7 = 7,8 = 8,9 = 10; 7,13 = 3.5; 7,13′ = 3; 10,15 = 7; 14,14′ = 18; **5**: 11,13 = 7; *O*-Cinn 2′,3′ = 16.



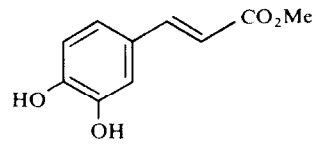
1



	2	3	4
R	H	Ac	H
R′	Cinn	Cinn	Meacr



5



6

(PhCH=CHCO$_2$H + 1, 100). 5 mg **2** were heated for 1 hr in 0.1 ml Ac_2O. TLC afforded 5 mg **3**, colourless gum; ^{1}H NMR, see Table 1.

Hyporadiolide-8-O-[2-*methylacrylate*] (**4**). Colourless gum, IR (CCl_4) cm^{-1}: 3620 (OH), 1780 (lactone), 1715, 1645 (C=CCO$_2$R, C=CCO); MS (CI, isobutane): 347 ($M^+ + 1$, 95%) ($C_{19}H_{22}O_6$); 261 ($M - RCO_2H$, 100).

11,13-*Dihydrohyporadiolide*-8-O-[2-*methylacrylate*] (**5**). Colourless gum, not free from **4**, IR (CCl_4) cm^{-1}: 3620 (OH), 1780 (lactone), 1715, 1645 (C=CCO$_2$R, C=CCO); MS (CI, isobutane): 349 ($M^+ + 1$, 100%); ($C_{19}H_{24}O_6$); 263 ($M - RCO_2H$, 85).

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