Phytochemistry, Vol. 21, No. 2, pp. 460–461, 1982.
Printed in Great Britain.

0031-9422/82/020460-02$03.00/0

A FURTHER SESQUITERPENE LACTONE ESTERIFIED WITH A SESQUITERPENIC ACID*

FERDINAND BOHLMANN, RAJINDER K. GUPTA and JASMIN JAKUPOVIC

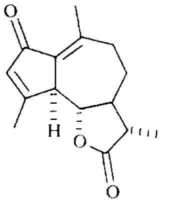
Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany

(*Received* 8 *April* 1981)

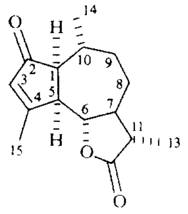
Key Word Index—*Hypothoeris oligocephala*; Compositae; sesquiterpenes; dihydrolactucin-C_{15}-ester; sesquiterpenic acid.

Abstract—The roots of *Hypochoeris oligocephala* afforded in addition to known compounds a further sesquiterpene lactone esterified with a sesquiterpenic acid as well as the corresponding free acid.

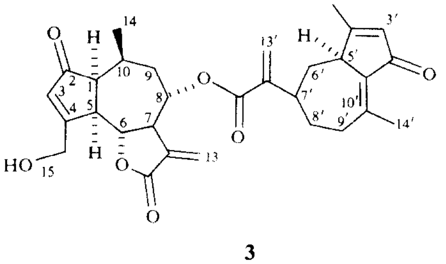
Hypochoeris oligocephala (Svent. et Bramwell) Lack. has also been placed in the monotypic genus *Heywoodiella* (subtribe Crepidinae)[1]. As *Hypochoeris glabra* afforded some unusual sesquiterpene lactones, a chemical investigation of *H. oligocephala* was of interest. A small sample collected on Tenerife afforded several compounds, which may be useful chemotaxonomic markers. The roots contained lupeyl acetate, desacetoxymatricarin (**1**) [2] and **2**, which could be identical with carpesia lactone [3], where no stereochemistry at C-10 and C-11 was reported. The ^1H NMR data (Table 1) indicated both methyls as α-oriented, as $J_{1,10}$ and $J_{7,11}$ was 11 Hz. As carpesia lactone has been correlated with guaiol the stereochemistry at C-10 would be different from that of **7** [4]. The more polar fractions afforded the acid **4**, which we have named isohypoglabric acid. Its structure clearly followed from the ^1H NMR data (Table 1). A second compound was a further sesquiterpene lactone esterified with a sesquiterpenic acid, which most probably was **3**. The mass spectrum clearly gave the molecular formula $C_{30}H_{34}O_7$ with fragments at m/z 260 ($M - RCO_2H$) and m/z 246 ($C_{15}H_{18}O_3$), which corresponded with the ion of the acid **4**. The ^1H NMR data (Table 1) of the acid part were similar to those of **4** and those of the lactone moiety were close to those



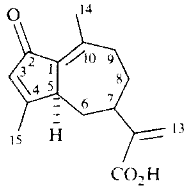
1



2



3



4

---

*Part 376 in the series "Naturally Occurring Terpene Derivatives". For Part 375, see Bohlmann, F., Ahmed, M., Borthakur, N., Wallmeyer, M., Jakupovic, J., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 167.

Table 1. ^{1}H NMR spectral data of compounds **2**–**4** (400 MHz, $CDCl_3$, TMS as int. standard)

	2	**4**	**3**		
H-1	1.93 *dd*	—	2.50 *m*	H-3′	6.05 *dq*
H-3	5.93 *dq*	6.05 *dq*	6.42 *dt*	H-5′	3.14 *br d*
H-5	2.82 *br dd*	3.14 *br d*	3.32 *br dd*	H-7′	2.84 *m*
H-6	3.78 *dd*		4.40 *dd*	H-13$'_1$	6.22 *br s*
H-7	1.74 *m*	2.85 *m*	3.20 *dddd*	H-13$'_2$	5.61 *br s*
H-8	1.8–1.6 *m*	2.0 *m*	5.27 *ddd*	H-14′	2.04 *br s*
H-9				H-15′	2.36 *br s*
H-10	2.16 *m*	—	2.02 *m*		
H-11	2.27 *dq*	—	—		
H-13	1.26 *d*	6.31 *br s*	6.32 *d*		
H-13′		5.60 *br s*	5.77 *d*		
H-14	1.23 *d*	2.37 *br s*	0.99 *d*		
H-15	2.25 *br s*	2.05 *br s*	4.78 *br dd*		
H-15′			4.62 *br dd*		

J(Hz): compound **2**: 1,5 = 5.5; 1,10 = 11; 3,5 = 3,15 = 1.5; 5,6 = 6,7 = 10; 7,11 = 11; 10,14 = 7; 11,13 = 6.5; compound **3**: 1,5 = 7; 3,5 = 3,15 = 1.5; 5,6 = 11; 6,7 = 9.5; 7,8 = 10; 7,13 = 3.3; 7,10′ = 2.8; 8,9 = 10; 8,9′ = 4; 10,14 = 7; 15,15′ = 18; 15, OH = 5; 3′,5′ = 3′,15′ = 1.5; 5,6 = 12; compound **4**: 3,5 = 3,15 = 1.5.

of lactucin. However, the olefinic methyl signal was replaced by a doublet indicating the presence of a 1,10-dihydro derivative. Though the stereochemistry at C-10 could not be determined with certainty, the chemical shift of H-14 indicated a β-orientation of the methyl, especially if compared with the shift in **1**, where the corresponding signal was shifted downfield due to the deshielding effect of the carbonyl group at C-2. As could be visualized from models only an α-methyl group should be deshielded by this keto group. The aerial parts gave sitosterol, stigmasterol, lupeol, its acetate as well as 16β-hydroxylupeol [5]. The lactone **3** isolated from the roots showed that *H. oligocephala* indeed could be transferred to *Hypochoeris*, as this type of lactone seems to be characteristic for the genus. However, the isolation of the rare flavone isoetin in a distinctive glycosidid form from the same plant supports its placement in its own genus [6].

EXPERIMENTAL

The air-dried plant material (voucher 81/1479, deposited in the Herbarium of the Institute) was extracted with Et_2O–petrol, 1:2 and the resulting extracts were separated first by CC (Si gel) and further by TLC (Si gel). Known compounds were identified by comparing the IR and ^{1}H NMR spectra with those of authentic material. The roots (15 g) afforded 2 mg lupeyl acetate, 2 mg **1**, 2 mg **2**, 0.5 mg **3** (Et_2O–petrol, 3:1) and 0.5 mg **4** (Et_2O–petrol, 1:1), while the aerial parts (200 g) gave 100 mg lupeol, 50 mg of its acetate, 10 mg lup-10-en-3β,16β-diol, 80 mg sitosterol and 50 mg stigmasterol.

'*Carpesia lactone*' (**2**). Colourless gum, MS *m/z* (rel. int.): 248 $[M]^+$ (52) ($C_{15}H_{20}O_3$), 233 $[M-Me]^+$ (24), 123 (62), 96 (100).

1,10-*Dihydrolactucin*-8-*O*-*isohypoglabrate* (**3**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1785 (lactone), 1720 (CO_2R), 1700 (C=O); MS *m/z* (rel. int.): 506.230 $[M]^+$ (22)($C_{30}H_{34}O_7$), 270 $[M-RCO_2H]^+$(6), 246 $[\mathbf{4}]^+$(37), 228 $[246-H_2O]^+$(21), 200$[228-CO]^+$(44), 148 (100), 133 $[148-Me]^+$ (29).

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+46 \quad +49 \quad +54 \quad +104} (CHCl_3;\ c\ 0.5).$$

Isohypoglabric acid (**4**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745 (CO_2H), 1700 (C=O); MS *m/z* (rel. int.): 246.126 $[M]^+$(6)($C_{15}H_{18}O_3$), 58 (100). $[\alpha]_D$ + 6 ($CHCl_3$; *c* 0.5).

Acknowledgements—We thank Dr. Lack, Botanical Museum, Berlin-Dahlem, for identification of plant material and the Deutsche Forschungsgemeinschaft for financial support.

REFERENCES

1. Tomb, A. S. (1977) In *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.) p. 1067. Academic Press, New York.
2. Gonzales, A. G., Bermejo Barrera, J., Massanet, G. M., Amarao, J., Dominguez, B. and Morales, A. (1976) *Phytochemistry* **15**, 991.
3. Kariyone, T., and Naito, S. (1956) *J. Pharm. Soc. Jpn* **75**, 39.
4. Naito, S. (1955) *J. Pharm. Soc. Jpn* **75**, 323.
5. Baddely, G. V., Bealing, A. J., Jefferies, P. R. and Retallack, R. W. (1964) *Aust. J. Chem.* **17**, 908.
6. Harborne, J. B. (1978) *Phytochemistry* **17**, 915.