^{13}C NMR (Table 1) and MS {m/z 368 $[M]^+$(1.2%), the remaining spectrum was almost identical with that of **2**} spectra and comparisons with lit. data [1].

6β-Cinnamoyloxy-1β-hydroxy-7α(H)-11,12-dihydroeremophil-9-ene (**2**). Isolated from CC fr. 10 (2.17 g). The residue was resubmitted to silica gel CC (50 g, packed dry). Elution with *n*-hexane containing 0–30% EtOAc under vacuum gave 15 frs. Fr. 11 (240 mg), which showed one major spot on TLC, when submitted to PLC [*n*-hexane–EtOAc (4:1), 2 developments] gave **2** as a colourless foam, characterized as 6β-cinnamoyloxy-1β-hydroxy-7α(H)-11,12-dihydroeremophil-9-ene based on the spectral data described in the text.

Acknowledgements—We thank Dr Steven P. McLaughlin for plant collection and identification. This investigation was supported in part by the National Science Foundation under Grant No. PCM-8304771 which we gratefully acknowledge.

REFERENCE

1. Bohlmann, F., Grenz, M., Gupta, R., Dhar, A., Ahmed, M., King, R. and Robinson, H. (1980) *Phytochemistry* **19**, 2391.

Phytochemistry, Vol. 28, No. 11, pp. 3231–3232, 1989.
Printed in Great Britain.
0031–9422/89 \$3.00+0.00

FUROEREMOPHILANES FROM *HERTIA PALLENS*

J. Jakupovic, F. Bohlmann and M. Grenz

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, F.R.G.

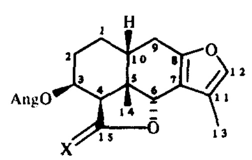
(*Received* 16 *February* 1989)

Key Word Index—*Hertia pallens*; Compositae; sesquiterpenes; furoeremophilane; eremophilanolides.

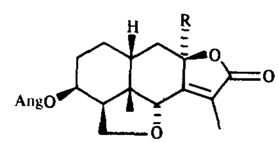
Abstract—The aerial parts of *Hertia pallens* afforded a new furoeremophilane and two eremophilanolides. The structures were elucidated by high field NMR spectroscopy. The proposed relationship of *Hertia* to *Othonna* is strongly supported by the chemistry.

INTRODUCTION

The twelve species of the genus *Hertia* (Compositae, tribe Senecioneae) are distributed over South and North Africa and South West Asia. The sterile disc styles indicate a close relationship to *Othonna* [1]. So far nothing is known on the chemistry of these plants. Therefore we have studied the constituents of *Hertia pallens* Kuntze. The results are discussed in this paper.



1 X = H_2
1a X = O

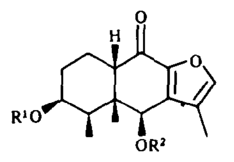


2 R = H
3 R = OH

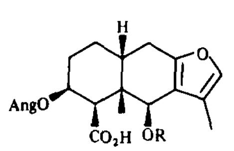
RESULTS AND DISCUSSION

The extract of the aerial parts afforded germacrene D, tremetone, oleanolic acid and the corresponding ketone, the furoeremophilanes **1** [2], **4** [3], **5** [4], **6** [4], **7** [5], **8**, **9** [3], **10** [4] and **11** [3] as well as the lactones **1a** [3] **2** and **3**.

The structure of **2** followed from its ^1H NMR spectrum (Table 1) where all signals could be assigned by spin decoupling. The couplings of H-10 indicated the presence of a *cis*-decalin derivative. Inspection of a model showed that H-6 must be β-orientated. The same is true for compound **1** where the configuration at C-6 has to be revised compound **31** in ref. 2.



	4	**5**	**6**	**7**	**8**
R^1	Ang	Ang	Sen	Ang	MeBu
R^2	Ang	Sen	Ang	*i*Bu	Ang



9 R = Sen
10 R = Ang
11 R = *i*Bu

Table 1. ^1H NMR spectral data of compounds **2**, **3** and **8** (400 MHz, $CDCl_3$, δ-values)

H	2	3	8*
1	2.17 *m*	2.16 *m*	2.18 *m*
1'	1.48 *m*	1.45 *m*	1.85 *m*
2	1.86 *br d*	1.87 *br d*	1.72 *m*
2'	1.64 *tt*	1.60 *tt*	
3	5.26 *q*	5.28 *q*	5.17 *br q*
4	2.03 *ddd*	2.00 *m*	1.90 *m*
6	4.44 *q*	4.54 *q*	6.33 *br s*
8	4.62 *ddq*	—	—
9	2.22 *dt*	2.16 *m*	—
9'	1.48 *m*	1.75 *t*	—
10	2.12 *m*	2.33 *br dt*	2.75 *br dd*
13	1.99 *t*	1.99 *t*	2.03 *d*
14	1.37 *s*	1.38 *s*	1.27 *s*
15	3.94 *t*	3.92 *t*	0.98 *d*
15'	3.70 *dd*	3.71 *dd*	
OAng	6.10 *qq*	6.09 *qq*	6.02 *qq*
	2.00 *dq*	2.00 *dq*	1.98 *dq*
	1.90 *dq*	1.91 *dq*	1.92 *dq*

*OMeBu: 2.43 *tq*, 1.85 *m*, 1.48 *ddq*, 0.89 *t*, 1.19 *d* (*J* [Hz]: 2, 3 = 2, 3' = 2, 5 = 7; 3, 3' = 14; 3, 4 = 3', 4 = 2, 5 = 7).

J[Hz]: Compounds **2** and **3**; 1, 2 = 1, 2' = 2.5; 1', 2 = 3; 1', 2' = 2, 2' = 14; 2, 3 = 2', 3 = 3, 4 ~ 2.5; 4, 15 = 15, 15' = 8; 4, 15' = 11; 6, 13 = 1.5; 8, 9 = 5; 8, 9' = 11; 8, 13 = 1; 9, 9' = 13 (compound **3**; 1, 10 = 9, 10 ~ 4; 9, 9' = 9', 10 = 13; 1', 10 = 1.5); compound **8**; 1, 10 = 4; 1', 10 = 6; 2, 3 = 2', 3 = 3, 4 ~ 3.5; 4, 15 = 7; 12, 13 = 1; (H-12 7.39 *q*); OAng: 3, 4 = 7; 3, 5 = 4, 5 = 1.5.

The ^1H NMR spectrum of **3** (Table 1) differed from that of **2** by the absence of a H-8 signal indicating that a hydroxy group may be at C-8. In agreement with this assumption the fragment in the mass spectrum at *m/z* 262 corresponds to $C_{15}H_{18}O_4$ which must be due to loss of angelic acid. Inspection of a model shows that hydroxy group in β-configuration should influence the chemical shift of H-6.

The structure of compound **8** was deduced from its ^1H NMR spectrum (Table 1) which was very similar to that of **6**. Comparison of the chemical shifts of H-3 and H-6 in the different diesters indicated that most likely a 6β-angeloyloxy derivative was present.

The chemistry of the *Hertia* species strongly supports the proposed close relationship of this genus to *Othonna* where furoeremophilanes of type **1**, **4**–**8** and **9**–**11** are widespread [5]. In particular, the compounds with oxygen functions at C-15 are only widespread in *Othonna.*

EXPERIMENTAL

The air-dried plant material (55 g, collected in August 1986 at the Franschhoek Pass, R.S.A., voucher 86/159, deposited in the Compton Herbarium, Kirstenbosch) was extracted at room temp with $MeOH–Et_2O$–petrol (1:1:1). Separation of the extract was achieved by CC (silica gel), TLC (silica gel) and finally HPLC RP 8, flow rate 3 ml/min, final conditions for new compounds in parenthesis). The following compounds were obtained: 4 mg germacrene D, 3 mg tremetone, 4 mg oleanolic acid, 5 mg of the corresponding ketone, 10 mg, **1**, 6 mg **1a**, 6 mg **2** (HPLC: $MeOH–H_2O$, 17:3, R_t 6.0 min), 5 mg **3** (HPLC: $MeOH–H_2O$, 17:3, R_t 5.5 min), 5 mg **4**, 5 mg **5**, 5 mg **6**, 5 mg **7**, 9 mg **8** (HPLC: $MeOH–H_2O$, 4:1, R_t 23.2 min), 3 mg **9**, 3 mg **10** and 9 mg **11**. Compounds were identified by comparing the 400 MHz ^1H NMR spectra with those of authentic material.

3β-Angeloyloxy-6α, 15-epoxy-10βH-eremophil-7(11)-en-12,8β-olide (**2**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (γ-lactone), 1720, 1650 ($C=CCO_2R$); MS *m/z* (rel. int.): 246.126 $[M - AngOH]^+$ (78) (calc. for $C_{15}H_{18}O_3$: 246.126), 231 $[246 - Me]^+$ (100), 217 $[246 - CHO]^+$ (26), 83 $[RCO]^+$ (71), 55 $[83 - CO]^+$ (69); $[\alpha]_D^{24°}$ $+12°$ ($CHCl_3$; *c* 0.34).

3β-Angeloyloxy-8α-hydroxy-6α, 15-epoxy-10βH-eremophil-7(11)-en-12,8β-olide (**3**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3590 (OH), 1765 (γ-lactone), 1720, 1645 ($C=CCO_2R$); MS *m/z* (*rel. int.*): 262.121 $[M - AngOH]^+$ (51) (calc. for $C_{15}H_{18}O_4$: 262.121), 247 $[262 - Me]^+$ (74), 229 $[247 - H_2O]^+$ (30), 83 $[RCO]^+$ (100), 55 $[83 - CO]^+$ (91); $[\alpha]_D^{24°}$ $+62°$ ($CHCl_3$; *c* 0.19).

3β-[2-Methylbutyryloxy]-6β-angeloyloxy-10βH-furoeremophil-9-one (**8**). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745 (CO_2R), 1730 ($C=CCO_2R$), 1695 ($C=O$); MS *m/z* (*rel. int.*): 430.236 $[M]^+$ (8) (calc. for $C_{25}H_{34}O_6$: 430.236), 346 $[M - O=C=C(Me)Et]^+$ (2), 246 $[346 - AngOH]^+$ (61), 85 $[C_4H_9CO]^+$ (52), 83 $[C_4H_7CO]^+$ (100), 57 $[85 - CO]^+$ (91), 55 $[83 - CO]^+$ (78).

Acknowledgement—We thank Dr J. Rourke (Kirstenbosch, R. S. A.) for identification of the plant material.

REFERENCES

1. Nordenstam, B. (1977) *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L. eds), p. 812. Academic Press, London.
2. Bohlmann, F. and Suwita, A. (1976) *Chem. Ber.* **109**, 1320.
3. Bohlmann, F. and Knoll, K.-H. (1978) *Phytochemistry* **17**, 461.
4. Bohlmann, F., Zdero, C. and Grenz, M. (1974) *Chem. Ber.* **107**, 3928.
5. Jakupovic, J., Pathak, V. P., Grenz, M. Banerjee, S., Wolfrum, C. and Bohlmann, F. (1987) *Phytochemistry* **26**, 1049.