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AN UNUSUAL NEROLIDOL DERIVATIVE FROM *ARTEMISIA INCULTA**

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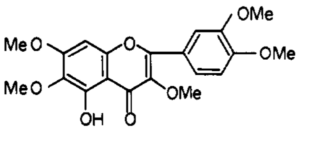
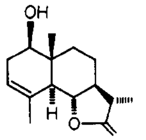
Key Word Index—*Artemisia inculta*; Compositae; sesquiterpene; nerolidol derivative; artemetin.

Abstract—The aerial parts of *Artemisia inculta* afforded a new nerolidol derivative named arteinccultone.

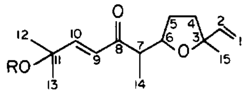
Artemisia inculta Del. grows in Saudi Arabia. Nothing is known on the chemistry of this species. Investigation of the aerial parts afforded the known flavone artemetin (**1**) [1], dihydrosantamarin (**2**) [2] and a highly oxygenated sesquiterpene, the hydroperoxide, **3**, which could be transformed to the corresponding alcohol, **4**, by treatment with triphenylphosphine. The ^{1}H NMR spectra of **3** and **4** (Table 1) clearly showed the presence of a vinyl end-group and a conjugated *trans*-double bond. The peroxy proton showed a singlet at δ 7.77. The secondary methyl group (1.09 *d*) was coupled with a proton which displayed a double quartet at δ 2.95. This chemical shift obviously required a proton α to a carbonyl group, the presence of which was indicated by the IR band at 1695 cm^{-1}. Spin decoupling, starting with the signal at δ 2.95 led to the sequence **A**.



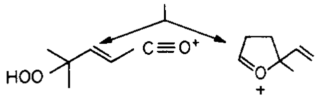
1



2

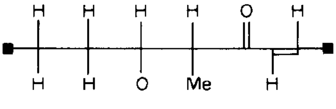


3 R = OH
4 R = H
m/z 268



5 *m/z* 129 (13)

6 *m/z* 111 (100)



A

Table 1. ^{1}H NMR spectral data of compounds **3** and **4** (400 MHz, CDCl$_3$, TMS as int. standard)

H No.	**3**	**4**
1	5.19 *dd*	5.13 *dd*
1′	5.00 *dd*	4.98 *dd*
2	5.91 *dd*	5.90 *dd*
4	1.90 *ddd*	1.91 *ddd*
4′	1.78 *ddd*	1.77 *ddd*
5	2.05 *dddd*	2.02 *dddd*
5′	1.70 *dddd*	1.68 *dddd*
6	4.15 *ddd*	4.23 *ddd*
7	2.95 *dq*	2.94 *dq*
9	6.41 *d*	6.43 *d*
10	6.85 *d*	6.92 *d*
12	1.44 *s*	1.41 s
13	1.42 s	
14	1.09 d	1.08 d
15	1.29 s	1.29 s
O–OH	7.77 *s*	—

J (Hz): 1*c*, 1*t* = 1.5; 1*c*, 2 = 10; 1*t*, 2 = 17; 4, 4′ = 12; 4, 5 = 9; 4, 5′ = 7; 4′, 5 = 7.5; 4′, 5′ = 4; 5, 5′ = 12; 5, 6 = 8.5; 5′, 6 = 6; 6, 7 = 8.5; 7, 14 = 7; 9, 10 = 15.5.

The remaining signals required, in addition to the vinyl group, three further tertiary methyls. Accordingly, **3** was the only logical structure as the small shift differences in the spectra of **3** and **4** strongly supported the proposed position of the dimethyl peroxy end-group. Also, the observed fragments **5** and **6** in the mass spectrum of **3** only agreed with this arrangement. The relative stereo-

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*Part 478 in the series "Naturally Occurring Terpene Derivatives". For Part 477 see Bohlmann, F., Jakupovic, J. and Schuster, A. (1983) *Phytochemistry* **22**, 1637.

chemistry at C-3, C-6 and C-7, however, could not be determined.

EXPERIMENTAL

The air-dried aerial parts (1 kg) collected from the 'Abha' region, Saudi Arabia, in Nov. 1981 were extracted continuously with petrol (bp 60–80°). The concentrates on standing in a refrigerator afforded a solid which was separated first by CC (Si gel) and further by TLC (Si gel). The fractions obtained with C_6H_6–EtOH (19:1) afforded 1 g **1**, 100 mg **2** (mp and ^{1}H NMR spectra of **1** and **2** identical with those of authentic material) and 7 mg **3**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (O_2H), 1695, 1635 (C=CC=O); MS *m/z* (rel. int.): 268.167 $[M]^+$ (0.5) ($C_{15}H_{24}O_4$), 235 $[M-O_2H]^+$ (3), 234 $[M-H_2O_2]^+$ (6), 129 $[C_6H_9O_3$ (**5**)$]^+$ (13), 111 $[C_7H_{11}O$ (**6**)$]^+$ (100). To 7 mg **3** in 1 ml $CDCl_3$ 10 mg triphenylphosphine was added. After 15 min, TLC (Et_2O–petrol, 1:1) afforded 6 mg **4**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1695, 1675, 1630 (C=CCO); MS *m/z* (rel. int.): 252.173 $[M]^+$ (2.3) ($C_{15}H_{24}O_3$), 237 $[M-Me]^+$ (15), 234 $[M-H_2O]^+$ (20), 216 $[234-H_2O]^+$ (5), 193 $[M-C_3H_7O]^+$ (11), 166 $[234-Me_2CO]^+$ (24), 142 $[MeCH=C(OH)CH=CHC(Me)_2OH$, McLafferty$]^+$ (23), 113 $[HO(Me)_2CCH=CHCO]^+$ (100), 111 $[$**6**$]^+$ (98);

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+49 \quad +53 \quad +62 \quad +130} \; (CHCl_3;\; c\ 0.6).$$

Acknowledgement—We thank Professor Dr. A. Migahad, King Saud University, Riyadh, for identification of the plant material.

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PSEUDOGUAIANOLIDES AND GUAIANOLIDES FROM *HELENIUM PUBERULUM**

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Key Word Index—*Helenium puberulum*; Compositae; sesquiterpene lactones; pseudoguaianolides; guaianolides.

Abstract—The aerial parts of *Helenium puberulum* afforded three new sesquiterpene lactones, two pseudoguaianolides and 2α-acetoxyhelenium lactone. The structures were elucidated by ^{1}H NMR spectroscopy. The stereochemistry of helenium lactone was determined by NOE measurements.

A reinvestigation [1] of the polar fractions of the aerial parts of *Helenium puberulum* (tribe Heliantheae, subtribe Gaillardiinae) [2] afforded helenium lactone (**1**) [3], helenalin (**3**) [4], mexicanin I (**4**) [5] and three further lactones, the guaianolide **2**, the 2α-acetoxy derivative of **1** and the pseudoguaianolides, **5** and **7**. The ^{1}H NMR spectrum of **2** was close to that of **1**. As, however, the stereochemistry of helenium lactone was not established, we studied the relative stereochemistry of **1** by NOE in deuteriobenzene which showed close *cis*-relationships of H-8 with H-1 and H-7, and vice versa, and of H-6α with H-7 and H-13'. Therefore, with the small coupling $J_{7,13}$ an 8,12-*cis*-lactone was present and H-1 was α-orientated. Though the NOE of H-5 could not be observed, as the corresponding signal was an overlapped multiplet, the coupling $J_{5,6\beta}$ clearly indicated that H-5 was also α-orientated. The chemical shift of H-15 agreed with a β-methyl group at C-4. Accordingly, the stereochemistry of helenium lactone was most likely as shown by structure **1**. The ^{1}H NMR spectral data of **2** differed from those of **1**, mainly by the additional lowfield signal at δ 5.25. Spin decoupling showed that this three-fold doublet had to be assigned to H-2β, if a model was considered. In agreement with this orientation, the H-1 signal was slightly shifted downfield. An H-1β epimer of **2**, pleniradin acetate, its configuration being established by X-ray analysis [6], showed typically different ^{1}H NMR signals [6]. In particular, the chemical shifts of H-1 and H-7 differed strongly.

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*Part 476 in the series "Naturally Occurring Terpene Derivatives". For Part 475 see Bohlmann, F., Brindöpke, G. and Vogel, W. (1982) *Justus Liebigs Ann. Chem.* 2041.