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GERMACRANOLIDES FROM *ANVILLEA GARCINI*

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Key Word Index— *Anvillea garcini*; Compositae; sesquiterpene lactones; germacranolides.

Abstract—The aerial parts of *Anvillea garcini* afforded three germacranolides, two of which had not being isolated previously. The structures were elucidated by ^{1}H NMR spectroscopy. The configuration of 9-acetoxy parthenolide at C-9 has been revised.

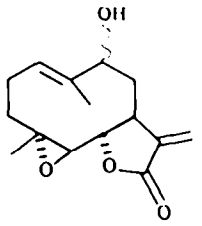
INTRODUCTION

The small genus *Anvillea* (tribe Inuleae, subtribe Inulinae) is placed in the Inula group [1]. From *A. garcini* (Burm.) DC flavones [2] and 9α-hydroxyparthenolide (**1**) [3] were reported. A reinvestigation of a sample collected in the South of Iran gave in addition to 9α-hydroxyparthenolide (**1**), two further lactones, **2** (the epimer of **1**) and **3** (the epoxide of **2**). The structures were elucidated by high field ^{1}H NMR spectroscopy.

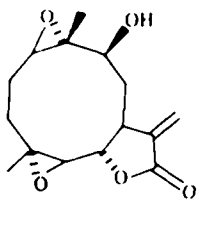
RESULTS AND DISCUSSION

The spectrum of **2** (Table 1) was in part close to that of **1**, apart from the H-9 signal which showed a very different splitting pattern. Spin decoupling allowed the assignment of all signals. Irradiation of the five-fold doublet at δ2.86 collapsed the H-13 doublets to singlets and therefore were due to H-7. The latter was further coupled with three-fold doublets at δ2.11 and 2.01. As the corresponding protons were further coupled with the double doublet at δ4.27 (H-9) and H-7 also was coupled with the triplet at δ3.86 (H-6), which itself collapsed to a doublet on irradiation of the doublet at δ2.69 (H-5) the whole sequence H-5–H-9 was settled. The signals of H-1–H-3 were nearly identical with those of **1**, accordingly, the structure and the stereochemistry of **2** were settled and the structure of a lactone from *Matricaria suffruticosa* which was errously given as the acetate of **2** [4] has to be revised to 9α-acetoxyparthenolide, the acetate of **1** as the couplings of H-9 are small.

The ^{1}H NMR spectrum of **3** (Table 1) indicated that this lactone had no olefinic double bonds. Spin decoupling allowed the assignment of all signals though a few were overlapping multiplets. A multiplet at δ2.83 (H-7) was coupled with the doublets at δ6.38 and 5.70 as well as with the triplet at δ3.94 (H-6), the threefold doublet at δ1.89 (H-8) and the multiplet at δ2.28 (H-8). A double doublet at δ3.28 was coupled with H-8 and therefore was due to H-9.



1 9α OH
2 9β OH



3

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

H	1	2	3
1	5.63 *d* (*br*)	5.42 *dd* (*br*)	2.93 *dd*
2α	2.28 *d* (*br*)	2.24 *d* (*br*)	2.23 *m*
2β	2.51 *ddd*	2.50 *ddd*	1.60 *m*
3α	1.30 *ddd*	1.23 *ddd*	1.36 *m*
3β	2.20 *ddd*	2.18 *ddd*	2.29 *m*
5	2.76 *d*	2.69 *d*	2.80 *d*
6	3.86 *t*	3.86 *t*	3.94 *t*
7	3.42 *ddddd*	2.86 *ddddd*	2.83 *m*
8α	2.38 *ddd*	2.21 *ddd*	2.28 *d* (*br*)
8β	1.93 *ddd*	2.01 *ddd*	1.89 *ddd*
9	4.35 *d* (*br*)	4.27 *dd*	3.28 *dd*
13	6.34 *d*	6.36 *d*	6.38 *d*
13′	5.65 *d*	5.68 *d*	5.70 *d*
14	1.72 *s* (*br*)	1.75 *s* (*br*)	1.40 *s*
15	1.30 *s*	1.33 *s*	1.37 *s*

J (Hz): compound 1: 1, 2α = 4; 1, 2β = 12; 2α, 2β = 13; 2β, 3α = 12; 2β, 3β = 5; 5, 6 = 6, 7 = 9; 7, 8α = 1.5; 7, 8β = 8; 7, 13 = 3.5; 7, 13′ = 3; 8α, 8β = 15; 8α, 9 = 6; 8β, 9 ~ 1; compounds 2 and 3: 1, 2α = 3; 1, 2β = 12; 2α, 2β = 13; 2β, 3α = 12; 2β, 3β = 5; 5, 6 = 6, 7 = 9; 7, 8α = 3; 7, 8β = 9; 7, 13 = 3.5; 7, 13′ = 3; 8α, 8β = 15; 8α, 9 = 2.5; 8β, 9 = 10.5; (compound 3: 1, 2α = 2; 1, 2β = 11).

The upfield shift of the latter, if compared with the shift in 2 indicated that the 1,10-double bond had been replaced by an epoxide. Accordingly, a double doublet at δ2.93 (H-1) and a singlet at δ1.40 were visible. The signals of the second epoxide moiety were a doublet at δ2.80 and a methyl singlet at δ1.37. The stereochemistry at all chiral centres followed from the couplings. Thus 3 was the epoxide of 2.

EXPERIMENTAL

The air dried aerial parts (300 g, collected 90 km north of the Persian Gulf, voucher 55/40, deposited in the Herbarium of the Dept. of Biological Science, University of Shahid Beheshty, Teheran, Iran) were extracted with Et_2O–petrol–MeOH (1:1:1). The resulting extract after removal of saturated long chain saturated hydrocarbons by treatment with MeOH was separated first by CC (silica gel). TLC (silica gel, PF 254, $CHCl_3$–MeOH, 25:1) of the polar fraction gave a mixture which by repeated TLC (Et_2O) afforded 150 mg 1 (R_f 0.58), 60 mg 2 (R_f 0.46) and 25 mg 3 (R_f 0.40).

9β-Hydroxyparthenolide (2). Colourless gum; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1775 (γ-lactone); MS *m/z* (rel. int.): 264.136 [M]$^+$ (1) (calc. for $C_{15}H_{20}O_4$: 264.136), 55 (100); $[\alpha]_D^{24°} = -37$ ($CHCl_3$; *c* 0.15).

9β-Hydroxy-1β,10α-epoxyparthenolide (3). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone); CIMS *m/z* (rel. int.): 281 [M + 1]$^+$ (100) ($C_{15}H_{20}O_5$ + 1), 263 [281 − H_2O]$^+$ (17); $[\alpha]_D^{24°} = -19$ ($CHCl_3$; *c* 0.05).

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