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SESQUITERPENE LACTONES FROM *SCHKUHRIA ANTHEMOIDEA* VAR. *WISLIZENII*

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Key Word Index—*Schkuhria anthemoidea* var. *wislizenii*; Asteraceae; Heliantheae; elemanolide; germacrolide.

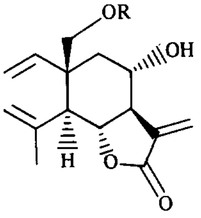
Abstract—We report here on the isolation and characterization of two new elemanolides and the known germacrolide 11,13-dehydroeriolin from *Schkuhria anthemoidea* var. *wislizenii*.

INTRODUCTION

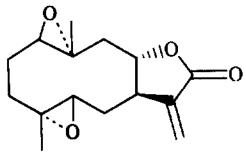
The taxonomically difficult genus *Schkuhria* Roth [1] has a diverse sesquiterpene lactone chemistry which includes germacrolides [2, 3], melampolides [4, 5], several heliangolides [3, 6–8] and an elemanolide [4]. As part of our continuing study of the sesquiterpene lactone chemistry of the Heliantheae, we report here two new elemanolides (**1** and **2**) and the known germacrolide 11,13-dehydroeriolin (**3**) from *Schkuhria anthemoidea* var. *wislizenii* (Gray) Heiser. The germacrolide **3** has also been reported from *Schkuhria schkuhrioides* [2, 4], *S. pinnata* [2] and *Carpesium abrotanoides* [9]. An earlier study of *Schkuhria anthemoidea* [3] reported heliangolides and germacranolides.

RESULTS AND DISCUSSION

The elemanolide **1** had a molecular formula of $C_{15}H_{20}O_4$ (HRMS: 264.13615 calculated, 264.13580 measured). An IR absorption at 1762 cm^{-1} suggested that an α,β-unsaturated γ-lactone moiety was present in the compound. Signals in the ^1H NMR spectrum for the exocyclic methylene protons (H-13a and H-13b) [10] were observed at $\delta 6.30$ ($J = 2.1$ Hz) and 5.94 ($J = 1.5$ Hz); according to Samek [10–12] these are characteristic for *cis* fused α,β-unsaturated γ-lactones. Other elemanolides also follow Samek's empirically derived rule correlating the magnitude of the 7,13-coupling and the stereochemistry of lactone ring fusion [10–12]: for example, in epitulipdienolide, a *trans* fused elemanolide, $J_{7,13a} = 3.2$ Hz and $J_{7,13b} = 3.0$ Hz [13]; while in isoepitulipdienolide, a *cis* fused elemanolide, $J_{7,13a} = 1.4$ Hz and $J_{7,13b} = 1.4$ Hz [13]. Double irradiation experiments showed that the two protons H-13a and H-13b were coupled to a multiplet at $\delta 2.91$ (H-7) which was coupled to a doublet of doublets at $\delta 3.80$ (H-6) and to a doublet of doublets at $\delta 4.75$ (H-8). The signal at $\delta 3.80$ (H-6) was also coupled to a doublet at $\delta 2.23$ (H-5). The signal, at $\delta 4.75$ (H-8), was further coupled to doublets of doublets at $\delta 2.19$ (H-9a) and 1.86 (H-9b). The chemical shift of H-8 ($\delta 4.75$), the IR absorption at 3594 cm^{-1} and the fact that there were no signals for a side chain (NMR and MS) suggested that a hydroxyl was located at C-8. The geminal coupling between H-13a and H-13b as well as the chemical shifts for these protons suggested that the 8-hydroxyl was in the α orientation [10]. Further decoupling experiments established that the doublet of doublets at $\delta 5.77$ (H-1) was coupled to signals at $\delta 5.21$ (H-2a) and $\delta 5.12$ (H-2b). Doublets at $\delta 5.21$ (H-3a) and $\delta 4.86$ (H-3b) were allylically coupled to a vinyl methyl at $\delta 1.86$. This coupling established the position of the second hydroxyl at C-14 rather than C-15 and thus distinguished **1** from the known 11(13)-dehydromeliten-



1 R = H
2 R = Ac



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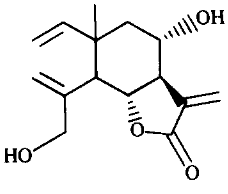

4

Table 1. ^1H NMR spectra of **1** and **2** (270 MHz, $CDCl_3$, TMS as an int. standard)

H	1	2
1	5.77 *dd*	5.78 *dd*
2a	5.21 *d*	5.19 *d*
2b	5.12 *d*	5.12 *d*
3a	5.21 *s* (*br*)	5.20 *s* (*br*)
3b	4.86 *s* (*br*)	4.85 *s* (*br*)
5	2.23 *d*	2.21 *d*
6	3.90 *dd*	3.90 *dd*
7	2.91 *m*	2.95 *m*
8	4.75 *ddd*	4.76 *ddd*
9a	2.19 *dd*	2.15 *dd*
9b	1.86 *dd*	1.93 *dd*
13a	6.30 *dd*	6.32 *dd*
13b	5.94 *dd*	5.98 *dd*
14a	3.66 *d*	4.15 *d*
14b	3.55 *d*	3.95 *d*
15	1.86 *s* (*br*)	1.85 *s* (*br*)
OAc	—	2.03 *s*

J (Hz): 1, 2a = 10.5; 1, 2b = 14.7; 5, 6 = 11.6; 6, 7 = 9.45; 7, 8 = 6.3; 8, 9a = 6.3; 8, 9b = 5.2; 9a, 9b = 14.7; 7, 13a = 2.1; 7, 13b = 1.5; 14a, 14b = 10.0.

sin (**4**) [14]. Spectral comparisons of a second new compound **2** with **1** clearly established that **2** was the acetate of **1**.

The known compound, 11,13-dehydroeriolin (**3**), also found in this *Schkuhria* species, was identified by comparison of spectral data with published values [2, 4, 9].

EXPERIMENTAL

Plant material. Leaves and flowers of *S. anthemoidea* var. *wislizenii* were collected by J. Gershenzon and J. Norris on November 25, 1981, at Jalisco, Mexico; 1.2 miles east off highway 44 south of Guadalajara on the road to Juanacatlan, west of Ejjdo de La Alameda. A voucher specimen (J.G. and J.N. #119) is on deposit in the Herbarium of the University of Texas at Austin.

Extraction and separation. Air-dried aerial parts (2.17 kg) were extracted with CH_2Cl_2 (42 l.) and worked-up in the usual manner [15]. The resulting extract (17.7 g) was charged on a silica gel column (450 g silica gel 60) which was eluted with a CH_2Cl_2–*iso*-PrOH gradient beginning with 100% CH_2Cl_2. Compound **1** was isolated from a fraction eluted from the column with CH_2Cl_2–*iso*-PrOH (99:1). It was further purified by prep. TLC (2 mm, silica gel; CH_2Cl_2–*iso*-PrOH, 15:1). Compounds **2** and **3** were obtained from another fraction eluted with CH_2Cl_2–*iso*-PrOH, 99:1). They were further purified by preparative TLC (2 mm, silica gel; petrol–EtOAc, 1:1).

Compound **1**. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3594, 3011, 2926, 1762, 1638, 1603, 1452, 1390, 1265, 1150, 1049, 1031, 980, 954, 909, MS *m/z*: 264, 246, 228, 216, 201, 183, 171, 159, 145, 133, 121, 105, 95, 91, 83, 69, 55, 43; ^{13}C NMR: δ170.1 *s*, 143.2 *s* + *t*, 138.3 *s*, 124.1 *t*, 115.2 *t*, 114.4 *t*, 75.0 *d*, 69.9 *d*, 64.9 *t*, 56.3 *d*, 46.4 *d*, 44.2 *t*, 32.6 *t*, 29.7 *q*, 26.0 *q*.

Compound **2**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3575, 3493, 3026, 2968, 2919, 1763, 1738, 1640, 1445, 1377, 1264, 1239, 1148, 1124, 1107, 1048, 1018, 957, 914; MS *m/z*: (no M + obs), 264, 246, 228, 216, 201, 200, 183, 171, 162, 159, 157, 145, 121, 107, 105, 95, 91, 83, 81, 69, 55, 43; ^{13}C NMR: δ170.8 *s*, 170.6 *s*, 142.3 *s* + *t*, 138.0 *s*, 124.3 *t*, 115.3 *t*, 114.2 *t*, 75.1 *d*, 70.0 *d*, 66.6 *t*, 56.0 *t*, 46.2 *d*, 41.8 *t*, 33.1 *t*, 29.7, 26.1 *q*, 20.8 *q*.

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