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FURTHER SESQUITERPENE LACTONES FROM *HELIANTHUS MAXIMILIANI*

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Key Word Index—*Helianthus maximiliani*; Asteraceae; sesquiterpene lactones; melampolide; heliangolide; germacrolide.

Abstract—By using HPLC, a new melampolide, a known heliangolide and three known germacrolides were isolated as minor constituents from a north central Texas population of *Helianthus maximiliani*. In an earlier report, we identified the germacrolide desacetyleupaserrin as the principal sesquiterpene lactone from this population.

INTRODUCTION

Three distinct sesquiterpene lactone chemical races of *Helianthus maximiliani* Schrader have been established by TLC surveys [1; Gershenzon, J., Stewart, E. and Mabry, T. J., unpublished results]. The principal sesquiterpene lactone constituents of each race have been characterized in earlier studies [2–5]. Heliangolides were found in a Kansas population [2] and guaianolides from a South Texas collection [3] while the germacrolide desacetyleupaserrin (**1a**) along with two diastereoisomers of 8-β-epoxyangeloyloxy-2-α-hydroxy-costunolide (**1b** and **1c**) and the novel dilactone **2** were found in a north central Texas population [4, 5].

Because *H. maximiliani* has been selected for biological studies, we have looked for the minor sesquiterpene lactones by using semi-preparative HPLC and have thus isolated five such constituents from the central Texas population: a novel melampolide **3**, a known heliangolide niveusin C (**4**) and three known germacrolides (**1d–1f**). Niveusin C (**4**) has also been reported from *Helianthus niveus* subspecies *canescens* [6], *H. annuus* [7, 8] and from the heliangolide-producing chemotype of *H. maximiliani* [2]. One of the known germacrolides, **1d**, has been reported from *Tithonia rotundifolia* [9] and *Helianthus resinosus* [10]. The germacrolide mollisorin A (**1e**) has previously been found in *Helianthus mollis* [11]; the known germacrolide **1f** has been isolated from *Eupatorium mikanioides* [12] and *H. resinosus* [10].

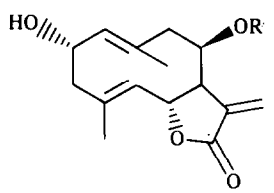
RESULTS AND DISCUSSION

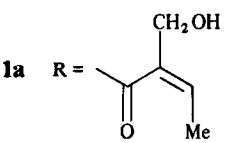
Spin decoupling established the proton sequence of the melampolide **3** and except for the chemical shift of H-8 and the side chain signals of **5** the spectral properties of **3** correspond to those of the known melampolide **5** [13] (see Table 1). The signal at δ5.25 (H-8) was coupled to doublets of doublets' at δ2.70 (H-9a) and 2.05 (H-9b), as well as a multiplet at δ2.35 (H-7). The chemical shift of H-8 (5.25), the Ir absorbance at 3365 cm^{-1} and the fact that there were no signals for a side chain (NMR and MS) suggested that there was a hydroxyl at H-8. Since the 7,8-coupling of **3** (2 Hz) was the same as for **5** [13] and the signals for H-13a and H-13b exhibited only doublet multiplicity the 8-hydroxyl could be assigned a β-orientation.

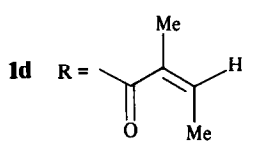
The known compounds reported here were identified by comparison of spectral data with published values [6, 9, 11, 12].

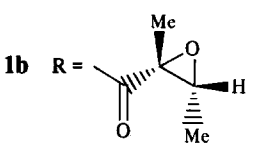
EXPERIMENTAL

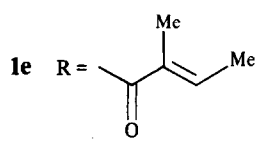
Plant material. Leaves and flowers of *H. maximiliani* were collected by J. Gershenzon and E. S. Stewart on September 4,

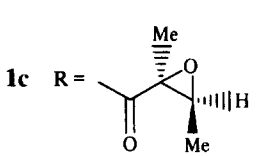


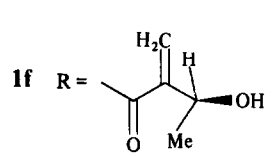


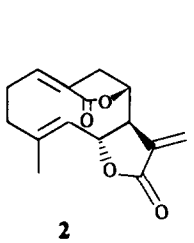












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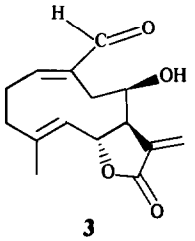

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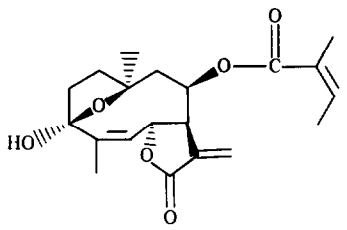

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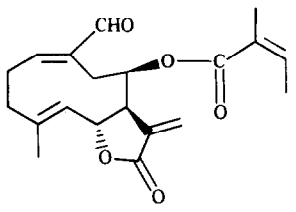

5

Table 1. ^{1}H NMR spectral data of compound 3 (200 MHz, $CDCl_3$, TMS as int. standard)

H	3
1	6.58 *dd*
2a	2.50 *m*
2b	2.18 *m*
3a	2.40 *m*
3b	2.00 *m*
5	5.03 *m*
6	5.11 *dd*
7	2.35 *m*
8	5.25 *ddd*
9a	2.70 *dd*
9b	2.05 *dd*
13a	6.30 *d*
13b	5.57 *d*
14	9.40 *s* (*br*)
15	1.94 *s* (*br*)

J (Hz): 3: 5,6 = 10.5; 6,7 = 10; 7,8 = 2; 8,9a = 6.5; 8,9b = 9.5; 9a,9b = 14; 7,13a = 3.2; 7,13b = 4.2.

1981, 5 miles north of Caradan (Mills Co), TX. A voucher specimen (J.G. #200) is on deposit in the Herbarium of the University of Texas at Austin.

Isolation. In our initial investigation [4] of a central Texas population of *H. maximiliani* a CH_2Cl_2 extract of dried leaves and flowers was chromatographed over silica gel. Elution with 100% CH_2Cl_2 yielded the previously reported germacrolide desacetyleupaserrin (**1a**) as the principal sesquiterpene lactone constituent; in addition, two diastereoisomers of 8-*β*-epoxy-angeloyloxy-2-*α*-hydroxy-costunolide, mollisorin B (**1b**) and its 2′*R*,3′*R* diastereoisomer **1c**, and the novel dilactone **2** [5] were also isolated. A later fraction, also eluted with 100% CH_2Cl_2 from the initial silica gel column, was shown by TLC to contain several minor sesquiterpene lactone constituents. This fraction was reinvestigated. It was further purified by using reverse phase HPLC (C-18, ultrasphere ODS; 25 cm × 10 mm id; UV detector 254 nm; H_2O–MeOH–MeCN, 10:7:3), to yield compounds **1a**–**1f**, **3** and **4**.

Compound **3**. IR ν_{max} cm^{-1}: 3365, 3024, 2933, 1762, 1679, 1624, 1458, 1391, 1302, 1243, 1142, 1035, 982, 872; MS *m/z*: 262, 244, 215, 203, 179, 161, 133, 105, 91, 84, 83, 69, 55, 43; ^{13}C NMR: 154.2 (C-1), 26.4 (C-2), 37.3 (C-3), 143.2 (C-4), 126.8 (C-5), 74.7 (C-6), 50.9 (C-7), 64.4 (C-8), 31.5 (C-9), 136.8 (C-10), 138.0 (C-11), 170.0 (C-12), 120.0 (C-13), 195.5 (C-14), 17.2 (C-15). HRMS: 262.12050 calc.; 262.12149 obs.

The reported known compounds were identified by comparison of spectral data with published values.

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