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A SESQUITERPENE DILACTONE FROM *HELIANTHUS MAXIMILIANI*

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Key Word Index—*Helianthus maximiliani*; Asteraceae; Heliantheae; sesquiterpene dilactone; maximileolide; decoupling difference spectroscopy; NOE difference spectroscopy.

Abstract—A new sesquiterpene dilactone, maximileolide, has been isolated from *Helianthus maximiliani* and its structure determined by high field NMR spectroscopy with the aid of difference spectroscopy techniques.

INTRODUCTION

Three distinct sesquiterpene lactone chemical races of the widely distributed perennial sunflower *Helianthus maximiliani* Schrader have been established by TLC surveys [J. Gershenzon, E. S. Stewart and T. Mabry, unpublished results]. The principal sesquiterpene lactone constituents of each race have been characterized in earlier studies [1–3]. As part of an extended study of *Helianthus maximiliani*, we report here a novel sesquiterpene dilactone, maximileolide, from a north central Texas population. In an earlier report [1], we identified the germacranolide desacetyleupacerrin as the principal sesquiterpene lactone constituent of this population. Two diastereoisomers of 8β-epoxyangeloyloxy-2α-hydroxycostunolide were also reported: mollisorin B and its 2′*R*,3′*R*-diastereoisomer.

Nuclear Overhauser enhancement difference spectroscopy (NOEDS) has recently been shown to be a technique of outstanding value in the establishment of spatial relationships within molecules [4] and its application to the structure elucidation of diterpenes has been demonstrated [5, 6]. We now describe the further application of this technique in the sesquiterpene field and also show that the information provided by this technique is complemented and extended by the use of decoupling difference spectroscopy (DDS).

RESULTS AND DISCUSSION

Maximileolide had a molecular formula $C_{15}H_{16}O_4$ (HRMS: 260.10423 measured, 260.10485 calculated). IR absorptions at 1772 and 1752 cm^{-1} suggested that two α,β-unsaturated γ-lactone moieties were present in the molecule. The characteristic doublets in the ^{1}H NMR spectra for the exocyclic methylene protons of an α,β-unsaturated lactone (H-13a and H-13b) were found at δ6.34 ($J = 3.8$ Hz) and 5.64 ($J = 3.0$ Hz) and were observed in the high field (400 MHz) ^{1}H NMR spectrum to be further split ($J = 0.8$ Hz) by mutual coupling. The magnitude of the coupling constants indicated that the lactone was *trans*-fused. Double irradiation experiments showed that these two protons were coupled to a proton at δ2.86 (H-7) which was coupled to a double doublet at 4.82 (H-6). The latter signal was coupled to a doublet at 4.54 (H-5) which was in turn allylically coupled to the only methyl signal in the ^{1}H NMR spectrum, a vinyl methyl at δ1.75. Further decoupling experiments established that the signal at δ5.84 (H-1) was coupled to signals at 3.16 (H-2a) and 2.42 (H-2b), which were themselves extensively coupled. The downfield position of H-8, (δ5.09) suggested that there was an ester attachment at this position. However, since there was no evidence for a side chain

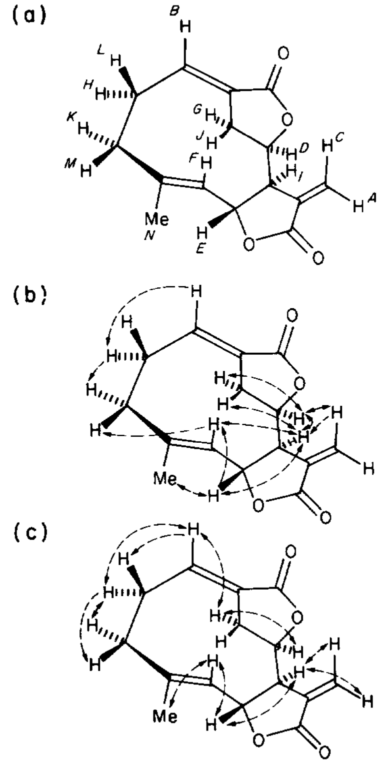

Fig. 1. Structure of maximileolide (a) and illustration of major interactions in NOEDS (b) and DDS (c)

Table 1. 400 MHz ^{1}H NMR of maximileolide and results of NOEDS and DDS

Proton	δ CDCl$_3$	*J* (Hz)	Protons enhanced in NOEDS	Protons decoupled in DDS
A	6.34 *dd*	0.8, 3.8	C	C, I
B	5.84 *m*			G, H, L
C	5.64 *dd*	0.8, 3.0	A, D, I	A, I
D	5.09 *d*	8.5	C, G, I	G
E	4.82 *dd*	10.0, 10.0	F, I, N	F, I
F	4.54 *dm*	10.0, ~1	I, M	E, N
G	3.46 *m*	2.5, 8.5, 14.5	D, J	B, D, J
H	3.16 *m*		B, K, L	B, K, L, M
I	2.86 *ddd*	3.0, 3.8, 10.0	E, F, J	A, C, E
J	2.66 *d*	14.5	G, I	G
K	2.48 *m*		M	H, M
L	2.42 *m*		not irradiated	
M	1.93 *m*		not irradiated	not irradiated
N	1.75 *d*	1.3	E	F

(NMR and MS), lactonization was indicated, most likely between C-14 and C-8. The ^{1}H NMR data therefore suggested structure **1** (Fig. 1). Further evidence supporting this structure was provided by the difference spectra (NOEDS and DDS), which assisted particularly in assignments of the complex multiplet due to the protons at C-2, C-3 and C-9 (Table 1). As in earlier work [4–6], the NOEDS and DDS results provide a three-dimensional network of inter-relationships between the protons (Fig. 1) which assist in the build-up of the assigned structure and give it a high degree of confidence.

EXPERIMENTAL

Plant material. Leaves and flowers of *Helianthus maximiliani* were collected by J. Gershenzon and E. S. Stewart, September 4, 1981, 5 miles north of Caradan (Mills Co.), Texas. Voucher specimen (J.G. 200) is on deposit in the Herbarium of the University of Texas at Austin.

Isolation. Reinvestigation of a crystalline precipitate isolated during our earlier work [1] from a fraction eluted with CH$_2$Cl$_2$ from the initial silica gel column yielded 5 mg of the new sesquiterpene lactone. MS (70 eV) *m/z*: 260, 242, 232, 214, 151, 110, 91, 81, 67, 55, 43. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 1772, 1752, 1669, 1659. ^{1}H NMR: see Table 1.

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