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A HELIANGOLIDE FROM *CHROMOLAENA GLABERRIMA*

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Key Word Index—*Chromolaena glaberrima*; Eupatorieae; Compositae; new heliangolide; 4′-dehydrochromolaenide

Abstract—The investigation of *Chromolaena glaberrima* afforded, besides the known heliangolide chromolaenide, a new 4′-dehydrochromolaenide. The structure of the new compound was elucidated by spectroscopic methods.

INTRODUCTION

As part of our continuing chemosystematic investigations of sesquiterpene lactones of the Compositae, we investigated *Chromolaena glaberrima* (DC.) King and H. Robins., a member of the subtribe Praxelinae of the tribe Eupatorieae [1]. Previous workers have reported the heliangolide chromolaenide from this species [2], the only germacrane-derived sesquiterpene lactone reported so far from the subtribe [3] We report herein a similar heliangolide (**2**) with a novel side chain.

RESULTS AND DISCUSSION

The major sesquiterpene lactone isolated from *Chromolaena glaberrima* was chromolaenide (**1**), which was previously reported [2, 4] from the same species ^{13}C NMR data, which had not been reported for **1**, is listed in Table 1.

We report here a new heliangolide, namely, 4′-dehydrochromolaenide (**2**). High-resolution mass measurement of the molecular ion (m/z 402) established the molecular formula of **2** as $C_{22}H_{26}O_7$. The presence of an aldehyde function in **2** was obvious from the IR (1690 cm^{-1}), ^{13}C NMR (aldehydic carbon signal at δ191.1) and ^{1}H NMR (aldehydic proton signal at δ10.17) spectral data The ^{1}H NMR spectrum of **2** (see Table 2) was essentially identical to that of **1** except that the two-proton signal at δ4.35 was replaced by the aldehydic proton signal at δ10.17 (d) and the methyl group of the side chain shifted downfield from δ1.8 to 2.3. The assignment of stereochemistry is based on the near identity of most of the NMR signals of **1** and **2** and on the co-occurrence of the compounds in *C glaberrima.*

Spin decoupling experiments were undertaken to confirm the structure of **2**. Irradiation at δ10.17, the frequency of the aldehydic proton, collapsed a multiplet at 6.75 (H-3′) to a narrow quartet. Reciprocally, irradiation at δ6.75 changed the doublet of the aldehydic proton at 10.17 and the signal for the methyl at 2.3 to singlets. In addition, irradiation at 2.3 simplified the multiplet at δ6.75 to a clear doublet, supporting coupling between the aldehydic and vinylic protons.

Since the aldehydic proton appeared at δ10.17 and the side chain methyl group at 2.3, the stereochemistry of the C-2′/C-3′ double bond was assigned the *E*-configuration. This is in agreement with previous observations that the chemical shift of aldehydic protons in *trans*-α,β-unsatu-

Table 1 ^{13}C NMR spectral data for compounds **1** and **2***

	1	**2**
C-1	125.3 *d*†	125.5 *d*†
C-2	29.5 *t*	29.6 *t*
C-3	76.9 *d*‡	76.8 *d*‡
C-4	137.7	137.3
C-5	126.5 *d*†	126.4 *d*†
C-6	78.7 *d*‡	78.8 *d*‡
C-7	48.5 *d*	48.4 *d*
C-8	76.9 *d*‡	75.6 *d*‡
C-9	43.4 *t*	43.3 *t*
C-10	136.6	134.9
C-11	135.6	134.3
C-12	170.1	169.7
C-13	124.7 *t*	124.9 *t*
C-14	19.4 *q*†	19.6 *q*†
C-15	23.0 *q*	23.1 *q*
C-1′	166.3	166.0
C-2′	127.4	126.8
C-3′	142.7 *d*	144.4 *d*
C-4′	59.6 *t*	191.1 *d*
C-5′	12.5 *q*	11.9 *q*
C-1″	169.9	169.5
C-2″	21.2 *q*	21.2 *q*

*Run at 22.6 MHz in $CDCl_3$ with TMS as internal standard. Assignments were made using off-resonance decoupling experiments and model compounds [7, 8]

†, ‡These assignments may be interchanged.

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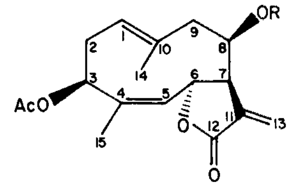

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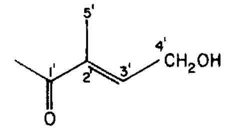

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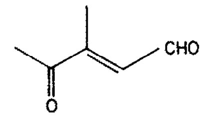

Table 2 ^{1}H NMR spectral data for compounds **1** and **2***

	1	2
H-1	5.27*m*	5.27*m*
H-2a	2.69*m*	2.69*m*
H-2b	2.29*m*	2.29*m*
H-3	5.27*t*	5.27*t*
H-5	5.22*dq* (*J* = 12, 1.3)	5.22*dq* (*J* = 12, 1.3)
H-6	5.96*dd* (*J* = 12, 1.8)	5.96*dd* (*J* = 12, 1.8)
H-7	2.98*m*	2.98*m*
H-8	5.27*m*	5.27*m*
H-9a	2.76*m*	2.76*m*
H-9b	2.45*m*	2.45*m*
H-13a	6.37*d* (*J* = 2.2)	6.37*d* (*J* = 2.2)
H-13b	5.78*d* (*J* = 2.0)	5.78*d* (*J* = 2.0)
H-14	1.8*d*	1.8*d*
H-15	1.82*d* (*J* = 1.8)	1.82*d* (*J* = 1.8)
H-3'	6.8*m*	6.75*m* (*J* = 12, 2)
H-4'	4.35*m*	10.17*d* (*J* = 13)
H-5'	1.8*d* (*J* = 1.3)	2.3*d* (*J* = 2)

*Run at 200 MHz in $CDCl_3$ with TMS as internal standard. Coupling constants in Hz

rated systems (*E*-form) generally appear at lower field ($\geq$ 10 ppm) than the same proton in *cis*-α,β-unsaturated systems, which usually appear at 9.26–9.4 [5]. This is the first report of this side chain.

EXPERIMENTAL

Extraction of Chromolaena glaberrima. Leaves (500 g) were collected by Alan Whittemore on 18 March 1982, between Tepic and Jalcocotan, Nayarit, Mexico (voucher in Herb TEX). The unground plant material was washed with CH_2Cl_2 and the extract worked up in the usual manner [6] The crude syrup obtained (7.5 g) was chromatographed on a silica gel column (160 g) packed in CH_2Cl_2 The column was eluted with a CH_2Cl_2–*i*-PrOH gradient, increasing the polarity with *i*-PrOH; 20 fractions of 300 ml each were collected. Fractions 7–11 (100% CH_2Cl_2) gave 500 mg **1** Fractions 13–16 (1% *i*-PrOH) gave compound **2** with a trace of **1**. Compound **2** was separated by prep. TLC (silica gel, 1.5 mm, CH_2Cl_2–*i*-PrOH, 15.1) to give 30 mg of an oily material.

Chromolaenide (**1**) This compound was previously isolated from *Chromolaena glaberrima* [2]. All the spectral data (MS, IR and ^{1}H NMR) and mp are consistent with the former report.

4'-Dehydrochromolaenide (**2**) MS (probe) 70 eV, *m/z* (rel. int.): 402 $[M]^+$ (4), 289 $[M - OHC–CH{=}C(Me)CO_2]^+$ (84), 288 $[M - OHC–CH{=}C(Me)COOH]^+$ (9.5), 228 $[288 - HOAc]^+$ (100), 97 $[OHC–CH{=}C(Me)CO]^+$ (91) IR $\nu_{max}^{CHCl_3}$ cm^{-1} 2950 (aldehyde C–H), 1760 (lactone C=O), 1690 (aldehyde C=O), UV λ_{max}^{MeOH} nm (log ε): 213 (2200).

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