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A HELIANGOLIDE FROM *CALEA LANTANOIDES*

WALTER VICHNEWSKI, ENIO GARCIA GOULART* and WERNER HERZ†

Nucleo de Pesquisas de Produtos Naturais do Faculdade de Farmácia e Odontologia, 14.100 Ribeirão Preto, São Paulo, Brazil; *Instituto de Ciências Biomedicas da Universidad Federal do Rio de Janeiro, Rio de Janeiro, Brazil; †Department of Chemistry, The Florida State University, Tallahassee, FL 32306, U.S.A.

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Key Word Index—*Calea lantanoides*; Compositae; Heliantheae; sesquiterpene lactone; heliangolide.

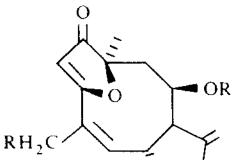
Abstract—An extract of *Calea lantanoides* which inhibits larval development of *Strongyloides stercoralis* and three species of hookworms gave the heliangolide 15-deoxybudlein A.

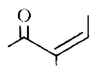
INTRODUCTION

A hexane–ethyl acetate extract of *Calea lantanoides* Gardn. (subtribe Neurolaeninae) showed inhibitory activity in the initial larval stages of *Strongyloides stercoralis* and three species of Ancylostomidae [1]. In an attempt to isolate the active principle, the crude extract was chromatographed and yielded a solid fraction which was identified as a heliangolide, 15-deoxybudlein A (**1a**).

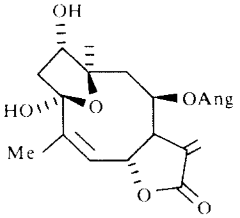
RESULTS AND DISCUSSION

The crystalline material, mp 132–134°, $C_{20}H_{22}O_6$ (high resolution MS) had IR bands at 1765 and 1660 cm^{-1} (α-methylene-γ-lactone), 1710 and 1590 cm^{-1} (dihydrofuran-3-one) and 1715 and 1650 cm^{-1} (α,β-unsaturated ester). The ^{1}H NMR spectrum (see Experimental) showed that the substance was the angelyl analogue **1a** of dienones **1b**, **1c** and **1d** which have been isolated from other Heliantheae [2–4] and thus the 15-deoxy derivative of budlein A(**1e**) [5, 6].‡ This was confirmed by analysis of the ^{13}C NMR spectrum (Table 1).



1a R=H,R'= 

1b R=H,R'=MeAcr
1c R=H,R'=isoBu
1d R=H,R'=isoVal
1e R=OH,R'=Ang



2

Table 1. ^{13}C NMR spectrum of **1a** (67.9 MHz, CDCl$_3$)

Carbon		Carbon	
1	204.99 *s*	11	138.72 *s**
2	103.00 *d*	12	168.68 *s*
3	184.86 *s*	13	123.51 *t*
4	131.76 *s**	14	21.20 *q*
5	134.08 *d*	15	20.02 *q*†
6	75.37 *d*	1′	165.68 *s*
7	48.49 *d*	2′	126.48 *s*
8	74.09 *d*	3′	140.97 *d*
9	41.98 *t*	4′	15.72 *q*
10	87.47 *s*	5′	19.42 *q*†

*,†Assignments may be interchanged.

A substance which was assigned formula **1a** but did not crystallize was obtained recently [7] in small quantity by treatment of **2** from *Helianthus maximiliani* with Jones reagent. Direct comparison of the IR and NMR traces showed that the two samples were identical. The previously unreported CD curve of **1a** (see Experimental) shows that **1a** and the heliangolides from *Helianthus maximiliani* possess the absolute configurations shown in the formulae.

EXPERIMENTAL

C. lantanoides was collected by Dr. Hermogenes de Freitas Leitão Filho in Serra do Caraça, Minas Gerais, Brazil, in December 1978 (Voucher No. VEC-9520 on deposit in the herbarium of UNICAMP). Extraction of the aerial parts (4.1 kg) with hexane–EtOAc (5:1) gave 33.3 g of crude extract which inhibited the larval development of *Strongyloides stercoralis* and three species of Ancyclostomidae. The material was chromatographed over 800 g of Si gel, 400-ml fractions being eluted as follows: fractions 1–5, hexane; 6–12, hexane–EtOAc (20:1); 13–29, hexane–EtOAc (10:1); 30–39, hexane–EtOAc (20:3); 40–49, hexane–EtOAc (5:1); 50–55, hexane–EtOAc (5:1); 56–61, hexane–EtOAc (10:3); 62–68; hexane–EtOAc (5:2); 69–74, hexane–EtOAc

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‡For conclusive proof that these substances are heliangolides and possess the C-8 stereochemistry shown in **1b–1e**, see Chowdhury, P. K., Sharma, R. P., Thyagarajan, G., Herz, W. and Govindan, S. V. (1980) *J. Org. Chem.* **45**, 4993.

(2:1); 75–85, EtOAc and 86–91, EtOH. Fraction 61 solidified and was recrystallized from C_6H_6 to give 110 mg **1a**, mp 132–134°. IR bands as given in the Discussion; ^{1}H NMR ($CDCl_3$) (identified by spin decoupling): δ 5.59 (H-2), 5.93 *dq* (4, 1.5 Hz, H-5), 5.3 *tq* (4, 1.5 Hz, H-6), 3.70 *m* (H-7), θ5.25 *ddd* (5.5, 4, 2 Hz, H-8), 2.53 *dd* (15, 5.5 Hz, H-9a), 2.29 *dd* (15, 4 Hz, H-9b), 6.36 *d* (3 Hz, H-13a), 5.69 *qd* (3 Hz, H-13b), 1.48 (3H, H-14), 1.80 *quint* (3p, 1.5 Hz, H-15), 5.11 *qq* (7, 1.5 Hz, H-3′), 1.93 *dq* (3p, 7, 1.5 Hz, H-4′), 1.80 *quint* (3p, 1.5 Hz, H-5′); CD (MeOH): $[\theta]_{323}+5900$ ($\Delta\epsilon$ + 1.79), $[\theta]_{288}-5220$ ($\Delta\epsilon-1.58$), $[\theta]_{256}+3000$ (sh, $\Delta\epsilon$ 10.91), $[\theta]_{236.5}+6700$ ($\Delta\epsilon+2.03$). [Calculated for $C_{22}H_{22}O_6$; MW, 358.1415. Found: MW (MS), 358.1427.]

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NOTE ADDED IN PROOF

Compound **1a**, also in noncrystalline form, has been reported recently among the lactone constituents of *Calea pilosa* and *C. morii* (Bohlmann, F., Fritz, W., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 743).

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LABDANE DERIVATIVES FROM *PLANALTOA LYCHNOPHOROIDES*[*]

FERDINAND BOHLMANN, CHRISTA ZDERO, HAROLD ROBINSON[†] and ROBERT M. KING[†]

Insitute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany; [†] Smithsonian Institution, Washington, DC 20560, U.S.A.

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Key Word Index—*Planaltoa lychnophoroides*; Compositae; Eupatorieae; diterpenes; *ent*-labdane derivatives; toxol derivative.

Abstract—The investigation of a representative of the small Brazilian genus *Planaltoa* afforded, in addition to known compounds, a new toxol derivative and two *ent*-labdane derivatives, closely related to austrofolin. The structures were elucidated by high field ^{1}H NMR spectroscopy. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

In continuation of our chemosystematic studies of the tribe Eupatorieae, we have now studied the constituents of *Planaltoa lychnophoroides* Barroso, one of the two Brazilian species of the genus belonging to the subtribe Alomiinae [1]. The aerial parts afforded germacrene D, bicyclogermacrene, α-humulene, lupeyl acetate, stigmasterol, the dehydronerolidol derivatives **3**[2] and **4**[3], the euparin derivative **5**[4], the toxol derivative **7**[5] and the corresponding dimethyl ether **8**, the structure of which followed from the molecular formula and the ^{1}H NMR data (see Experimental). The configuration at C-2 and C-3 was deduced from the coupling $J_{2,3}$, while the position of the methoxy groups clearly followed from the chemical shift of the aromatic proton. The polar fractions afforded two diterpenes, the *ent*-labdanes **10** and **11**. The structures of which followed from the ^{1}H NMR data (Table 1), the molecular formulae and

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[*] Part 386 in the series "Naturally Occurring Terpene Derivatives". For Part 385, see Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21**, 147.