

PRESENCE OF THE BORNYL ESTER OF DECA-2E,6Z,8E-TRIENOIC ACID IN *HELIOPSIS LONGIPES* ROOTS

JORGE MOLINA-TORRES,* RAFAEL SALGADO-GARCIGLIA, ENRIQUE RAMIREZ-CHAVEZ,

Departamento de Biotecnología y Bioquímica de Plantas, CINVESTAV-IPN, Unidad Irapuato, Apdo. Postal 629, CP 36500, Irapuato, Guanajuato, Mexico

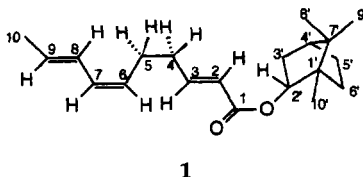
and ROSA E. DEL RIO

Instituto de Investigaciones Químico Biológicas, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Michoacan, Mexico

ABSTRACT.—A lipophilic extract of *Heliopsis longipes*, a plant collected from the wild and used for medicinal and insecticidal purposes, afforded a new compound, the bornyl ester of deca-2E,6Z,8E-trienoic acid [**1**], which was characterized by spectroscopic methods.

Heliopsis longipes (Gray) Blake has been used as an insecticide and for medicinal purposes (1) and is still widely used as a condiment in the areas of its natural occurrence. To satisfy previous commercial demand, plants were collected from the wild, since a large supply of *H. longipes* roots was required given the presence of the insecticidal amide, affinin (*N*-isobutyl-deca-2E,6Z,8E-trienamide). However, no detailed studies of other components in this species have been carried out. *H. longipes* now has a restricted distribution and hence has been substituted in commerce by other species of the same genus that are more widely distributed in North America, such as *H. helianthoides* (2), and more recently by species of *Echinacea*. *Heliopsis* belongs to the tribe Heliantheae and the family Compositae.

Our present objective was to study the compounds in *Heliopsis longipes* that could account for the prevailing use of this species as a flavoring and insecticidal plant. *H. longipes* roots afforded a new compound identified as the bornyl ester of deca-2E,6Z,8E-trienoic acid [**1**], [α]_D -32.35°. The compound showed no evidence of an NH signal at 3500 cm⁻¹ in the ir spectrum. The structure assignment of **1**, based on ¹³C- and ¹H-nmr data (Table 1), was confirmed using COSY and HETCOR nmr spectroscopy, and by comparison with model compounds such



1

as affinin [**3**] (3). The stereochemistry of the bornyl moiety (1R,2S) was deduced by comparing the ¹³C-nmr data of **1** with literature values (4), which agree with the observed optical activity and that reported for bornyl ferulate (5).

Decadiene and decatriene derivatives, mainly amides, are chiefly distributed in species of the Compositae, characteristically in the tribes Heliantheae and Anthemideae (6,7). These amides have been isolated from the roots, flower heads, and occasionally from the aerial parts of their plants of origin. Olefinic alkamides are considered to be of taxonomic value.

To our knowledge, this is the first report of an olefinic acid characteristic of the alkamides of *Heliopsis* species that is esterified to a monoterpene alcohol. Bornyl derivatives, mainly methyl esters, are frequently found in essential oils and are widespread in different families of monocotyledons and dicotyledons.

EXPERIMENTAL

PLANT MATERIAL.—Specimens of *Heliopsis longipes* were collected in July 1994, from Xichu, Sierra Gorda, Guanajuato, Mexico. Voucher speci-

TABLE 1. ^{13}C - and ^1H -Nmr Data of Compound 1.^a

^{13}C		^1H	
Position	δ mult.	Position	δ mult. (J_{HH} , Hz)
1	167.13 s	2	5.87 d (15.61)
2	122.40 d	3	6.96 dt (15.61, 6.60)
3	147.99 d	4	2.46–2.29 m
4	32.31 t	5	2.46–2.29 m
5	26.27 t	6	5.27 dt (10.6, 7.0)
6	127.51 d	7	5.99 t (10.91)
7	129.85 d	8	6.30 br dd (15.0, 10.91)
8	126.86 d	9	5.71 dq (15.0, 6.5)
9	130.20 d	Me-10	1.78 br d (6.5)
10	18.29 q	2'	4.93 ddd (9.99, 3.60, 2.10)
1'	48.98 s	3' α	2.46–2.29 m
2'	79.76 d	3' β	1.00 dd (13.72, 3.60)
3'	36.90 t	4'	1.68 m
4'	45.10 d	5' α	1.74 m
5'	28.12 t	5' β	1.31 m
6'	27.28 t	6' α	2.27–1.90 m
7'	47.91 s	6' β	1.23 m
8'	18.92 q	Me-8'	0.92 s
9'	19.77 q	Me-9'	0.88 s
10'	13.52 q	Me-10'	0.84 s

^a ^{13}C -Nmr multiplicity was obtained by a DEPT experiment.

mens were deposited in the Instituto de Ecología AC, Patzcuaro, Michoacan, Mexico, where taxonomic characterization was accomplished by Dr. J. Rzedowski.

EXTRACTION AND ISOLATION.—As described by Bauer *et al.* (8), *H. longipes* roots (500 g) were freeze-dried and macerated using a mortar and pestle, then extracted overnight with EtOAc. The extract was filtered and evaporated under reduced pressure. The extract was repeatedly purified by tlc on precoated Si gel plates (Sigma) developed with *n*-hexane/EtOAc. Purified fractions were analyzed by lrms (Hewlett-Packard model 5972 MSD) coupled to capillary gc (Hewlett-Packard GC model 5890, column HP Ultra 2; 25 m \times 0.02 mm i.d.; 0.33 μm film thickness). Finally, compounds were isolated by hplc on a Waters RP-18 column eluted with MeCN-H₂O (4:6) as described by Raldugin and Pentagova (8). ^1H - and ^{13}C -nmr spectra were recorded in CDCl₃ at 200 MHz on a Varian model Gemini 200 instrument. Ir spectra were obtained with a Perkin-Elmer model 599P spectrometer, uv spectra with a Varian model Cary 3E spectrometer, and optical rotations with a Perkin-Elmer polarimeter model 241.

Deca-2E,6Z,8E-trienoic acid bornyl ester [**1**].— $[\alpha]_{\text{D}} -32.35^\circ$; uv λ max (MeOH) 227 nm; ir ν max 1710, 1660 cm^{-1} ; m/z 302 (0.23) $[\text{C}_{20}\text{H}_{30}\text{O}_2]^-$

$[\text{M}]^+$, 137 (53), 109 (14), 93 (16), 81 (100) $[\text{C}_8\text{H}_9]^+$, 79 (18), 55 (15); ^1H - and ^{13}C -nmr data (CDCl₃), see Table 1.

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