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HELIANGOLIDES FROM *ISOCARPHA OPPOSITIFOLIA* VAR. *ACHYRANTHES*

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Key Word Index—*Isocarpha oppositifolia* var. *achyranthes*; Compositae; sesquiterpene lactones; heliangolides.

Abstract—A new heliangolide and the known compounds hiyodorilactone F and eucannabinolide have been isolated form *Isocarpha oppositifolia* var. *achyranthes*.

INTRODUCTION

The taxonomic position of the tropical American genus *Isocarpha* (Compositae) which comprises ten species [1] is still a matter of discussion. Its position in the Eupatoriae tribe seems to be in good agreement with its morphological and chemical characteristics [2, 3]. The presence of 3 (2, H) furanone heliangolides in *I. atriplicifolia* [4] seemed to support its placement in the Heliantheae tribe [5], but these types of compounds, which are frequent in Heliantheae, has been found also in members of the Eupatoriae tribe [6–8].

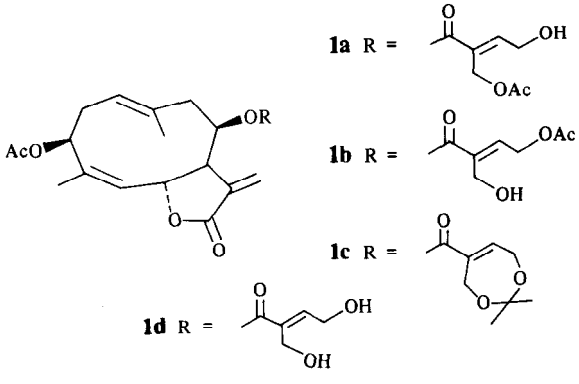
The chemical study of *Isocarpha oppositifolia* var. *achyranthes* collected in Northeastern, México, afforded germacranolides related to eucannabinolide, a type of compound common to both Eupatorieae and Heliantheae tribes.

RESULTS AND DISCUSSION

The aerial parts of *I. oppositifolia* (L.) Cass var. *achyranthes* (DC.) Keyland Stuessy afforded the known compounds hiyodorilactone F (**1a**) [9] and eucannabinolide (**1d**) [4]. The new heliangolide **1b** was found mixed with its isomer hiyodorilactone F (**1a**). The separation of the two compounds was very difficult.

The spectral data of lactone **1b** are almost superimposable on those of hiyodorilactone F (**1a**) (see Experimental) since the structure of both isomeric compounds only differ in the position of the acetate group of the ester side chain, the latter containing the acetate at C-5′ and **1b** at C-4′.

Compound **1c**, $C_{25}H_{32}O_8$, which preceded eucannabinolide in the chromatography was shown to be its acetonide, probably formed in the isolation process. The identification of **1c** was achieved by direct comparison with an authentic sample of eucannabinolide acetonide.



*Contribution No. 736.

EXPERIMENTAL

Extraction and separation. Air-dried parts of *Isocarpha oppositifolia* (L.) Cass var. *achyranthes* (DC.) Keiland Stuessy (604.6 g) collected in Tamaulipas, México, 65 km north of Cd. Victoria, Hway 101, (voucher MEXU 369283, deposited in the Herbarium of the Instituto de Biología, UNAM) were extracted with CH_2Cl_2 and Me_2CO. The crude extract (49.7 g) was percolated over silica gel and eluted with heptane, CH_2Cl_2, Me_2CO and MeOH. The Me_2CO fraction was chromatographed over silica gel using a heptane–EtOAc gradient elution system. The heptane–EtOAc (65:45) fractions were rechromatographed over silica gel using hexane and increasing proportions of Me_2CO, yielding 300 mg of a mixture of nearly 1:1.5 parts of **1a** and **1b**. The heptane–EtOAc (3:7) fractions after several purifications on CC gave 241.2 mg of **1c** and 366.8 mg of **1d**.

Eucannabinolide-19-O-*acetate* (**1b**). Pale yellow oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500, 1755, 1740, 1730 and 1660. CIMS (CH_4) 200 eV, *m/z* (rel. int.): 463 $[M+1]^+$ (2.0), 403 $[M+1-HOAc]^+$ (3.7), 289 $[M+1-RCO_2H]^+$ (1.9), 229 $[M+1-RCO_2H-HOAc]^+$ (100), 157 $[RCO]^+$ (6.2), 115 $[157-C_2H_2O]^+$ (4.6). ^1H NMR (80 MHz, $CDCl_3$): δ1.8 (3H, *br s*, H-14), 1.85 (3H, *d*, *J* = 1.5 Hz, H-15), 2.05 (3H, s, OAc), 2.12 (3H, s, OAc), 3.0 (1H, *m*, H-7), 4.34 (2H, *br s*, H-20), 4.86 (2H, *d*, *J* = 7 Hz, H-19), 5.25 (4H, *m*, H-1, H-3, H-5 and H-8), 5.75 (1H, *d*, *J* = 1.5 Hz, H-13_b), 5.9 (1H, *dd*, *J* = 2.5, 11 Hz, H-6), 6.35 (1H, *d*, *J* = 2 Hz, H-13_a) and 6.75 (1H, *t*, *J* = 7, H-18). Compound **1a**: 4.44 (*d*, H-19), 4.85 (*br s*, H-20), 7.02 (*t*, H-18).

Eucannabinolide-18,19-O-*acetonide* (**1c**). Colourless oil, $[\alpha]_D$ −122.8° ($CHCl_3$; *c* 0.197); UV λ_{max}^{MeOH} nm: 205 (ε 17870). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1740, 1710 and 1659. EIMS 70 eV, *m/z* (rel. int.): 460 $[M]^+$ (3.3), 402 $[M-C_3H_6O]^+$ (2.2), 289 $[M-RCO_2]^+$ (17.3), 228 $[M-RCO_2H-HOAc]^+$ (36.9), 155 $[C_8H_{11}O_3]^+$ (14.81), 97 $[C_5H_5O_2]^+$ (57.6), 91 $[C_4H_{11}O_2]^+$ (32.1), 69 $[C_4H_5O]^+$ (34.6), 43 $[C_2H_3O]^+$ (100). ^1H NMR (80 MHz, $CDCl_3$): δ1.4 (6H, *s*, Me_2C), 1.75 (3H, *br s*, H-14), 1.82 (3H, *d*, *J* = 1.5 Hz, H-15), 2.06 (3H, *s*, OAc), 2.95 (1H, *m*, H-7), 4.35 (2H, *m*, H-20), 4.45 (2H, *m*, H-19), 5.25 (4H, *m*, H-1, H-3, H-5 and H-8), 5.72 (1H, *d*, *J* = 2 Hz, H-13_b), 5.85 (1H, *dd*, *J* = 2.5, 11 Hz, H-6), 6.32 (1H, *d*, *J* = 2.5 Hz, H-13_a), 6.75 (1H, *m*, H-18).

Acetonide of **1d**. A soln of 155.3 mg of **1d** in 35 ml of dry Me_2CO and 87 mg of *p*-TsOH was stirred for 2.5 hr at room temp. The mixture was poured into ice-H_2O, extracted with CH_2Cl_2, neutralized with $NaHCO_3$, dried over dry Na_2SO_4 and the solvent removed under red. pres. Purification of the crude product by percolation over Kieselgel G (hexane–Me_2CO, 7:3) gave 90.0 mg of the acetonide, which was identical to a sample of **1c**.

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