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GERMACRAN-5,14,6,12-DIOLIDES FROM *MIKANIA URTICIFOLIA*

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Key Word Index—*Mikania urticifolia*; Eupatorieae; Compositae; mikanolide analogues; sesquiterpene lactones; geranylnerol derivative.

Abstract—The aerial parts of *Mikania urticifolia* gave, in addition to the known sesquiterpene dilactones mikanolide, deoxymikanolide and miscandenin and a known geranylnerol derivative, the new substance anhydroscandenolide.

INTRODUCTION

In continuation of our study of Argentine *Mikania* species we have examined *M. urticifolia* Hook. *et* Arn., a species characteristic of the Chaco phytographical province, whose distribution ranges from southern Bolivia to the province of Córdoba and the western region of Entre Rios. Isolated were mikanolide (**1**), the main secondary metabolite, deoxymikanolide (**2**), miscandenin (**3**) a new dilactone **4** and the geranylnerol derivative **5**. The structure and stereochemistry of **4** were deduced by comparing its ^{1}H NMR spectrum (Table 1) with the spectra of other such dilactones and spin decoupling which established the sequences C-1 through C-3 and C-5 through C-9 as well as the attachment of the α-methylene-γ-lactone function to 6-7.

The new dilactone anhydroscandenolide (**4**) may be a precursor of **1** en route from scandenolide (**6**). Dilactones of the mikanolide type are common constituents of members of the *M. scandens* complex [1–3] and diterpene **5** has been isolated previously from *M. periplocifolia* [2] which is also a member of the complex.

EXPERIMENTAL

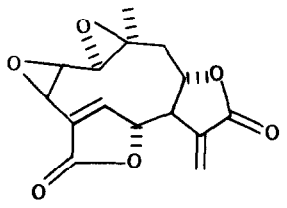
Aerial parts (1.1 kg) of *M. urticifolia* collected in March 1984 in the La Calera district, Departamento de Colón, Córdoba, Argentina, and identified by Dr Luis Ariza, Museo Botánico, Universidad Nacional de Córdoba, were extracted with $CHCl_3$. The usual work-up [4] gave 7.7 g of gum which was chromatographed on 250 g of silica gel packed in C_6H_6, 100 ml fractions being collected as follows: Frs 1–4 (C_6H_6), 7–10 (C_6H_6–Me_2CO, 19:1), 11–15 (C_6H_6–Me_2CO, 9:1), 16–20 (C_6H_6–Me_2CO, 4:1), 21–25 (C_6H_6–Me_2CO, 7:3), 26–30 (C_6H_6–Me_2CO, 3:2), 31–35 (C_6H_6–Me_2CO, 2:3), 36–40 ($CHCl_3$–MeOH 3:2), 41–45 (MeOH). Frs 16–20 after prep. TLC (C_6H_6–Me_2CO, 4:1) gave 70 mg of **1** [5, 6]; frs 33–37 on rechromatography (C_6H_6–Me_2CO, 4:1) afforded 78 mg of **5** [2]. Frs 41–45 (4.69 g) gave a positive test for alkaloids. Although fractionation and purification of the gum yielded traces of three basic substances, identification by spectroscopic means could not be achieved.

A second collection of *M. urticifolia* (March 1986, 1.25 kg) from the same location was extracted with MeOH by percolation at room temp. The combined extracts were evapd at red press. The residue was agitated with a 15% soln of citric acid, allowed to stand at room temp for 24 hr and filtered. The clear filtrate was washed with *n*-hexane; the hexane washings after drying and evapn yielded a syrup which on standing overnight in Et_2O deposited 800 mg of solid. The remaining extract after evapn of solvent afforded 1.33 g of gum. CC of the solid material (silica gel, C_6H_6 containing increasing amounts of Me_2CO) afforded 385 mg of **1**, 50 mg of a 1:1 mixture of **1** and **4**, 11 mg of **4**, 39 mg of a mixture of **3** and **4** and 90 mg of **3** [5, 6]. The gummy material after CC (silica gel, *n*-heptane containing increasing amounts of EtOAc) yielded 7.6 mg (after recrystallization from MeOH) of a 1:1 mixture of **1** and **3** [5, 7]. The aq. layer again gave a positive test for alkaloids but again no identifiable material.

Anhydroscandenolide (**4**), mp 73–75°; IR ν^{CHCl_3} cm^{-1} 1766; prep. CIMS *m/z* 275 $[M+1]^+$ (100%, only peak stronger than 5%).

Table 1. ^{1}H NMR spectrum of compound **4** ($CDCl_3$, 270 MHz)

H	**4**
1	3.76 *br d* (2)
2	6.14 *br d* (10.5, 2)
3	6.54 *dq* (10.5, 2)
5	7.46 *br d* (2)
6	5.43 *dt* (5, 2)
7	3.30 *dddd* (11, 5, 3.5, 3)
8	4.68 *ddd* (11, 10.5, 6)
9a	2.35 *dd* (14, 6)
9b	2.20 *dd* (14, 10.5)
13a	6.50 *d* (3.5)
13b	6.08 *d* (3)
14	1.18 *s* (3p)



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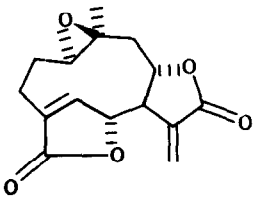

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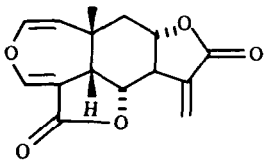

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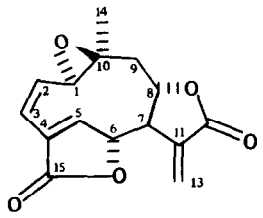

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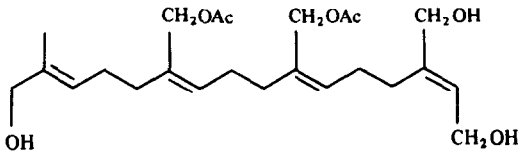

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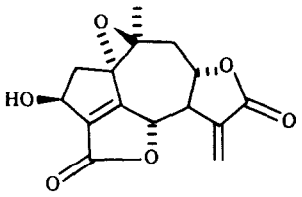

6

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