

SESQUITERPENE LACTONES FROM *MIKANIA MICRANTHA*

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Mikania micrantha H. B. K. (Compositae, tribe Eupatorieae) is chemically a variable species. Two collections from the Canal Zone (Panama) yielded mikanolide [**1**] and dihydromikanolide [**5**] (1), while a third collection from the same region gave the guaianolide mikanokryptin (1,2). Recently, mikanolide [**1**], deoxymikanolide [**2**], miscandenin, and three melampolides were isolated from material collected in Paraguay (3). As part of a study of Argentine Compositae we report here the chemical composition of *M. micrantha* collected in Tucumán, Argentina. Mikanolide [**1**], deoxymikanolide [**2**], scandenolide [**3**], dihydroscandenolide [**4**], dihydromikanolide [**5**], and the previously unreported dilactone anhydroscandenolide [**6**]¹ were identified in the CHCl₃ extract of this material. The hexane extract contained lupeol, α -amyrin, stigmaterol, and sitosterol.

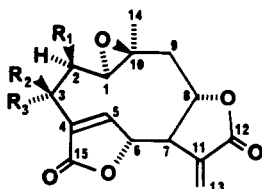
Compounds **1**–**5** were first isolated from *Mikania scandens* (5). The ¹H nmr of **6** (4) was similar to that of mikanolide

[**1**] except that it included two additional vinylic protons at δ 6.51 and 6.13 (CD₂Cl₂) replacing the signals corresponding to H-2 and H-3 in the spectrum of **1**. The ¹³C-nmr spectrum also supported the structure of **6**. The assignments are shown in Table 1. The previously unreported ¹³C-nmr data of **1**–**5** are included for comparison (Table 1).

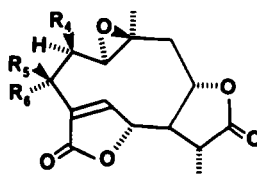
EXPERIMENTAL

PLANT MATERIAL.—Aerial parts of *M. micrantha* at the flowering stage were collected in Quebrada de Lules, Tucumán Province, Argentina, in May 1987 (voucher CANC 27 deposited in Instituto Miguel Lillo, S.M. de Tucumán).

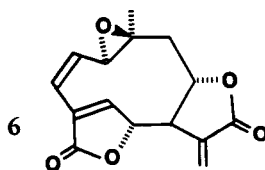
EXTRACTION OF *M. MICRANTHA*.—Dried flowers and leaves (47 g) were extracted with 2 \times 1 liter of CHCl₃ at room temperature for 7 days to give 3.77 g of extract (yield 8.0%). Trituration of the extract with EtOH (25 ml) at 55–60° gave a solution containing solid material. After cooling to room temperature, a white solid (51 mg) was obtained by decanting the supernatant. Repeated preparative tlc (Si gel, CHCl₃-hexane-MeOH, 20:10:1 and C₆H₆-EtOAc, 1:1) yielded **1** (22 mg), **2** (4 mg), and **5** (2.5 mg). The supernatant was diluted with H₂O (18 ml) and



- 1** R₁R₂=epoxy R₃=H
2 R₁=R₂=R₃=H
3 R₁=R₂=H R₃=OAc



- 4** R₄=R₅=H R₆=OAc
5 R₄R₅=epoxy R₆=H



¹After submission of this manuscript we learned that dilactone **6** has also been isolated from *Mikania urticifolia* by Gutierrez *et al.* (4).

TABLE 1. ^{13}C -Nmr Data of Compounds 1-6 (100.61 MHz, CD_2Cl_2).^a

Carbon	Compound					
	1	2	3	4	5	6
C-1	58.4 (d)	62.0 (d)	58.7 (d)	59.1 (d)	58.7 (d)	59.3 (d)
C-2	55.9 (d)	23.0 (t) ^b	29.6 (t)	29.4 (t)	55.4 (d)	151.4 (d)
C-3	50.6 (d)	22.3 (t) ^b	67.2 (d)	67.4 (d)	51.2 (d)	123.8 (d)
C-4	131.5 (s)	133.9 (s)	134.0 (s)	134.3 (s)	131.5 (s)	131.0 (s)
C-5	147.3 (d)	146.6 (d)	145.7 (d)	144.6 (d)	146.5 (d)	135.1 (d)
C-6	83.2 (d)	81.7 (d)	82.2 (d)	80.0 (d)	81.5 (d)	82.4 (d)
C-7	51.0 (d)	50.6 (d)	50.6 (d)	54.6 (d)	54.2 (d)	49.5 (d)
C-8	77.0 (d)	78.3 (d)	78.4 (d)	78.2 (d)	77.6 (d)	77.0 (d)
C-9	43.7 (t)	44.0 (t)	43.7 (t)	43.2 (t)	43.5 (t)	43.8 (t)
C-10	57.4 (s)	57.0 (s)	57.0 (s)	57.1 (s)	57.7 (s)	58.6 (s)
C-11	137.2 (s)	136.7 (s)	136.3 (s)	40.5 (d)	42.4 (d)	137.4 (s)
C-12	167.5 (s)	167.8 (s)	167.6 (s)	175.0 (s)	175.1 (s)	167.7 (s)
C-13	124.4 (t)	123.7 (t)	123.8 (t)	13.6 (q)	13.8 (q)	124.5 (t)
C-14	21.7 (q)	20.4 (q)	20.3 (q)	20.4 (q)	21.5 (q)	22.4 (q)
C-15	170.3 (s)	171.7 (s)	169.4 (s) ^b	169.4 (s) ^b	170.5 (s)	170.5 (s)
C-1'			169.5 (s) ^b	169.6 (s) ^b		
C-2'			21.1 (q)	21.1 (q)		

^aPeak multiplicity was determined by DEPT experiments.

^bAssignments in the same column with the same superscript are interchangeable.

extracted successively with hexane (3×40 ml) and CHCl_3 (3×40 ml). Evaporation of the hexane extract gave 1.94 g of residue that was dissolved in hexane-ErOAc (2:1), decolorized with charcoal, filtered, and chromatographed over Si gel using a hexane-Er₂O gradient. This afforded pentacyclic triterpenes (18 mg) and sterols (5 mg). Reversed-phase hplc of this triterpene fraction (Alltech RSil C-18 column, 10 mm i.d. \times 50 cm, 10 μm , MeOH at 3.5 ml/min) gave two peaks (ratio 3:1) corresponding to lupeol and α -amyrin, respectively. Separation of the sterol fraction gave stigmaterol and sitosterol (ratio 7:2). Sterols and triterpenes were identified on the basis of their relative retention times in gc and hplc. The identity of the sterols was also confirmed by determination of mp and mmp.

Evaporation of the CHCl_3 extract gave 850 mg of residue. Part of it (500 mg) was processed first by medium pressure layer chromatography (column packed with tlc-grade Si gel; C_6H_6 -ErOAc, 3:1). The fractions containing lactones (ir absorption at 1780 – 1740 cm^{-1}) were purified by repeated preparative tlc (C_6H_6 -ErOAc, 1:1 and 1:2; CHCl_3 -hexane-MeOH, 20:10:1) to give **1** (37 mg), **2** (10 mg), **3** (6 mg), **4** (8 mg), **5** (5.5 mg), and **6** (3 mg).

ANHYDROSCANDENOLIDE [**6**].—White crystals, mp 69 – 73° (without recrystallization); ir

(KBr) 1762 and 1662 cm^{-1} ; eims (Varian-MAT 112S) m/z (% rel. int.) [$\text{M} - \text{CHO}$]⁺ 245 (1), 241 (0.8), 227 (2.5), 217 (1.5), 213 (1.5), 199 (3.4), 138 (16), 135 (31), 121 (43), 110 (33), 108 (40), 95 (65), 85 (56), 80 (100). Microanalysis: C 65.70%, H 5.25%; $\text{C}_{15}\text{H}_{14}\text{O}_5$ requires C 65.69%, H 5.14%. ^1H -nmr (400 MHz) data were in good agreement with those in the literature (4) with the exception of differences due to the use of a different solvent (CD_2Cl_2). For ^{13}C -nmr data see Table 1.

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