

TERPENES OF *MIKANIA MONGENANSIS*

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Key Word Index—*Mikania mongenansis*; Compositae; terpenes; kaurenoic acid; dihydromikanolide.

Plant. *Mikania mongenansis*. The plant was first described by Badillo.¹ **Source.** Caripe, situated at an altitude of 600 m south east of Cumana. (Voucher specimen No. BHAT 00974 deposited in the University). **Uses.** Extracts of many *Mikania* species are used as folk medicine.² From *Mikania scandens* (L.) Willd. Herz *et al.*² have isolated sesquiterpenic dilactones belonging to the germacrane class, which are reported to exhibit tumor inhibitory activity.^{3,4}

Present work. The dried powdered plant was first exhaustively extracted with petrol. at room temp. followed by EtOH for 15 days. Each of these extracts were examined separately.

Petrol extract. The extract was chromatographed on silica gel and following fractions were collected: (1) petrol. (A₁); (2) benzene (A₂); (3) CHCl₃ (A₃); and (4) MeOH (A₄). From these fractions following compounds were isolated.

β -Pinene. The TLC of the petrol fraction (A₁) showed two major compounds and were separated by fractional distillation. The IR spectrum of lower boiling fraction was superimposable with that of the standard sample⁵ of β -pinene; also *R_f*s on TLC were comparable. The isolated compound showed following properties: b.p. 110–120° (bath)/0.8 mm; *n*_D²⁵, 1.4910; [α]_D –16.27° (CHCl₃); IR bands at 2950, 2920, 1650, 1470, 1460, 1380, 1370 and 885 cm^{–1} (Found: C, 88.43; H, 11.54. Calc. for C₁₀H₁₆: C, 88.23; H, 11.70%).

***n*-Ecosane.** The residue of the distillation was taken in Et₂O and on evaporation left gummy material which was crystallized from EtOH (95%) to give a compound identified as *n*-ecosane: m.p. 43–44°, lit.⁶ m.p. 36–37°. (Found: C, 85.47; H, 14.42. Calc. for C₂₀H₄₂: C, 85.10; H, 14.89%).⁷

(–)**Kaur-16-en-19-oic acid.** The benzene fraction (A₂) was further chromatographed on silica gel and following fractions were collected: (1) benzene (B₁); and (2) CHCl₃ (B₂).

¹ V. M. BADILLO, *Bol. Soc. Venezuelan cienc. Natur.* **10**, 300 (1946); also *Flora de Venezuela* (edited by L. ARISTEGUETA), Vol. X, Parts I and II, Instituto Botanica, Caracas, Venezuela (1964).

² W. HERZ, P. S. SUBRAMANIAM, P. S. SANTHANUM, K. AOTA and A. A. HALL, *J. Org. Chem.* **35**, 1453 (1970).

³ S. M. KUPCHAN, Y. AYNEHCHI, M. CASSADY, H. K. SCHONES and A. L. BURLINGAME, *J. Org. Chem.* **34**, 3867 (1969); S. M. KUPCHAN, Y. AYNEHCHI, M. CASSADY, H. K. SCHONES, A. T. MCPHAIL, G. A. SIM and A. L. BURLINGAME, *J. Am. Chem. Soc.* **88**, 3674 (1966).

⁴ H. YOSHIKA, T. J. MABRY and H. E. MILLER, *Chem. Commun.* 1679 (1968).

⁵ Standard sample of β -pinene was obtained from K & K Laboratories.

⁶ W. H. CAROTHERS, J. A. HILL, J. E. KIRBY and R. A. JACOBSON, *J. Am. Chem. Soc.* **52**, 5279 (1930).

⁷ Elemental analyses were carried out at M-H-W Laboratories, Garden City, Michigan, U.S.A.

The fraction (B_1) on concentration and cooling gave a white crystalline compound and was identified as (–)kaur-16-en-19-oic acid:^{8,9} m.p. 175–176°; $[\alpha]_D -98^\circ$ ($CHCl_3$); IR bands at 3070, 1770, 1260, 882 cm^{-1} . M^+ 302.2251 (M-Me, 42%; M- C_3H_7 , 51%; M- CHO_2 , 17.7%; M- CH_2O_2 , 14%; M- C_4H_{11} , 20%); two methyl singlet at 0.8 and 1.2 ppm and a two-proton signal centered at 4.77 ppm due to exocyclic methylene group. The fraction (B_2) gave the same compound.

EtOH extract. The EtOH extract was concentrated to a small vol. and then worked up following the method described by Geissman *et al.*¹⁰ The product obtained by this method was then chromatographed over alumina (activity I) and eluted as follows: (1) benzene- $CHCl_3$ (1:1) (C_1); (2) $CHCl_3$ (C_2); and (3) MeOH (C_3).

The fraction (C_1) on concentration gave a white solid identified as mikanolide,¹¹ m.p. and m.m.p. 221–222°. The IR spectrum showed prominent bands at 1765, 1752, 1676 and 1670 cm^{-1} . The $CHCl_3$ fraction (C_2) gave a solid which on repeated crystallization with $isoPr_2O-Me_2CO$ had m.p. and m.m.p. with an authentic sample¹¹ of dihydromikanolide 252–253°: IR bands at 1760 (very strong) and 1650 cm^{-1} (Found: C, 61.66; H, 5.36; Calc. for $C_{15}H_{16}O_6$: C, 61.53; H, 5.58%). To further confirm the presence of dihydromikanolide, acetic anhydride-*p*-toluene sulfonyl chloride re-arrangement² of the compound was carried out to give an acetate, which on MeOH-HCl hydrolysis gave the corresponding alcohol, m.p. 279–280°, identical to that described by Herz *et al.*² Of these two lactones dihydromikanolide is present as the major compound; we have not been able to isolate four other lactones (miscandenin, desoxymikanolide, scandenolide and dihydroscandenolide) so far from this plant; further work is in progress.

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⁸ C. A. HENRICK and P. R. JEFFERIES, *Austral. J. Chem.* **17**, 915 (1964).

⁹ D. E. U. EKONG, E. O. OLAGBEMI and F. A. ODUTOLA, *Phytochem.* **8**, 1053 (1969).

¹⁰ T. A. GEISSMAN, P. DEUEL, E. K. BONDE and F. A. ADDICOTT, *J. Am. Chem. Soc.* **76**, 687 (1954).

¹¹ The authors are extremely thankful to Professor W. HERZ, of Florida State University, for the precious gift of authentic samples of mikanolide and dihydromikanolide.