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SHORT COMMUNICATION

CONSTITUENTS OF *MIKANIA CORDATA* (BURM. F.) B. L. ROBINSON (COMPOSITAE)—II.*

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Abstract—In addition to mikanin, epifriedelinol and fumaric acid, previously isolated from *Mikania cordata*, we now report the isolation of stigmasterol, friedelin, glucose and fructose from the roots, and of mikanolide and dihydromikanolide from the leaves and stems of this plant.

Mikania cordata (Burm. f.) B. L. Robinson, the only Asiatic species of the genus, was for a long time considered to be conspecific with the introduced American species *M. scandens* (L.) Willd. non Hook. (FL. Br. Ind.).[1] Robinson,[2] however, redefined *M. cordata* and reaccepted specific rank for Asiatic plants. One year later he was followed by Koster,[3] who gave detailed descriptions for the Asiatic *M. cordata*, and the four formae distinguished by her within that species. The Malaysian species has recently been re-examined by P. Wycherley of the Rubber Research Institute of Malaya who concluded that it falls within *M. cordata*, and the plant is so named in the Institute's publications since 1964.

We had previously reported the isolation of a flavone, mikanin, together with epifriedelinol from the roots, and with fumaric acid from the leaves and stems of *M. cordata*.[4] Mikanin was characterized as 3,5-dihydroxy-4′,6,7-trimethoxyflavone, which has been synthesized by two methods.[5,6] The recent report on the presence of mikanolide and dihydromikanolide in the related species, *M. scandens* (L) Willd.,[7] prompts us to report on some additional products we have isolated from *M. cordata*.

The root powder was continuously extracted with (*a*) light petroleum and (*b*) methanol. The light petroleum extract yielded, in addition to mikanin and epifriedelinol, friedelin and stigmasterol. The methanol extract, besides giving mikanin, showed the presence of glucose and fructose.

The leaves and stems, dried and powdered, were extracted with (*a*) light petroleum and (*b*) ether. The ether extract has furnished the sesquiterpene lactones, mikanolide and dihydromikanolide, for which the structures I, and I hydrogenated at the terminal methylene have been proposed by Herz and his co-workers.[7]

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*Part I, *J. Chem. Soc.* 6371 (1965).

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[2] B. L. Robinson, *Contributions from Gray Herbarium, Harvard University*, **104**, 55 (1934); quoted by Wong Phui Weng, Ph.D. Thesis, University of Malaya (1965).

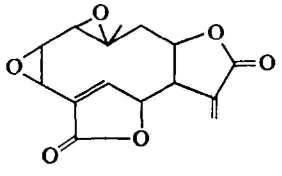
[3] J. Koster, *Blumea* 1, 503 (1935).

[4] A. K. Kiang, K. Y. Sim and J. Goh, *J. Chem. Soc.* 6371 (1965).

[5] K. Y. Sim, *J. Chem. Soc.* (c), 976 (1967).

[6] H. Wagner, L. Hörhammer, R. Hoer and L. Farkas, *Chem. Ber.* **100**, 1768 (1967).

[7] W. Herz, P. S. Santhanam, P. S. Subramanian and J. J. Schmid, *Tetrahedron Letters* 3111 (1967).



I

EXPERIMENTAL

M.p.s were taken on a Hoover capillary melting point apparatus. I.r. spectra were determined in Nujol, using a Perkin-Elmer 137 instrument. Light petroleum refers to the fraction of b.p. 56–70°.

Isolation of Mikanin, Friedelin, Epifriedelinol and Stigmasterol from the Roots; Presence of Glucose and Fructose

The root powder (2·8 kg) was continuously extracted with (*a*) light petroleum for 130 hr, and (*b*) methanol for 1 week.

(*a*) The solids containing crude mikanin, which appeared in the light petroleum extract, were filtered off. The filtrate was concentrated to a thick dark mass which was centrifuged and the light petroleum solution was decanted from the residue. Trituration of this residue with benzene gave a solid (0·70 g). A portion of this solid (0·18 g) was chromatographed on alumina (65 g) and yielded, on elution with light petroleum–benzene (6:1), a colourless product which recrystallized from chloroform as needles (20 mg), m.p. 258–260°, $[\alpha]_D -$ 19·1° (*c*. 1·78 in $CHCl_3$), having an identical i.r. spectrum as authentic specimen of friedelin; literature[8] gives m.p. 261–265°, $[\alpha]_D -$22° (*c*. 0·812 in $CHCl_3$). Further elution of the column with light petroleum-benzene (2:1) furnished epifriedelinol.[8]

The decanted light petroleum solution obtained above was fractionated into acidic and neutral fractions. The neutral fraction (10 g) was chromatographed on alumina (100 g). Elution with light petroleum gave epifriedelinol (48 mg). Further elution with benzene gave a colourless solid (0·39 g), which crystallized from chloroform–light petroleum in colourless needles, m.p. 161–164°, $[\alpha]_D -$53·6° (*c*. 2·39 in $CHCl_3$) (Found: C, 84·28: H, 11·85. Calc. for $C_{29}H_{48}O$: C, 84·40; H, 11·72%). The compound gave a deep green-brown colour in the Liebermann—Burchadt reaction and formed an acetate, m.p. 139–140° (from acetone–methanol), $[\alpha]_D$ −49·5° (*c*. 2·1 in $CHCl_3$) (Found: C, 81·62; H, 11·23. Calc. for $C_{31}H_{50}O_2$: C, 81·88; H, 11·08%). Literature[9] gives: stigmasterol m.p. 168–169°, $[\alpha]_D$ −47·3° (*c*. 1·36 in $CHCl_3$); and the acetate, m.p. 139–140°, $[\alpha]_D$ −54° (*c*. 1·78 in $CHCl_3$). The i.r. spectrum of the sterol was identical with that of authentic specimen of stigmasterol.

(*b*) The methanol extract was concentrated and the sticky residue was filtered off. Trituration of the residue with *n*-butanol yielded a yellow solid (1·78 g) which on recrystallization from methanol gave mikanin, m.p. 219–223°.

The methanol filtrate on further concentration gave a dark gummy residue which was stirred with water (400 ml) and the mixture filtered. The filtrate was extracted with ethyl acetate which gave mikanin (0·45 g). The aqueous layer was concentrated to a brown sticky mass (85·2 g) which gave a positive Molisch's test and reduced Fehling's solution. Paper chromatography[10] of this residue indicated the presence of glucose and fructose.

The aqueous concentrate (0·51 g) in water (5 ml) was treated with phenylhydrazine (0·35 g) in glacial acetic acid (5 ml). A small amount of yellow crystals was formed when the reaction mixture was heated for 2 min, but at the end of 4 min, a large amount of yellow solid (0·46 g), m.p. 204–206°, was obtained, which was identified as glucosazone by mixed m.p. and i.r. spectrum comparison with an authentic specimen.

Isolation of a Mixture of Mikanolide and Dihydromikanolide from the Leaves and Stems

The powdered material (1·2 kg) was exhaustively extracted with (*a*) light petroleum, and (*b*) ether.

(*a*) The light petroleum extract gave a dark waxy residue which is being examined.

(*b*) The solid (0·60 mg) remaining in the ether extract was filtered off and recrystallized from methanol–chloroform to give a colourless crystalline solid. The i.r. spectrum of this product showed that it consisted of a mixture of mikanolide and dihydromikanolide,[7] which was very difficult to separate by fractional crystallization.

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[8] P. R. Jefferies, *J. Chem. Soc.* 473 (1954).

[9] A. C. Ott and C. D. Bell, *J. Am. Chem. Soc.* **66**, 489 (1944).

[10] J. S. D. Bacon, J. Edelman, *Biochem. J.* **48**, 114 (1951).

The ether filtrate was concentrated and a brownish solid was collected and extracted with hot $CHCl_3$. The $CHCl_3$ extract yielded a mixture of mikanolide and dihydromikanolide which was filtered off and the filtrate evaporated to give a solid (0·61 g). A portion of this solid (0·30 g) was chromatographed on alumina (30 g) and elution with $CHCl_3$ furnished dihydromikanolide which crystallized from $CHCl_3$–methanol as colourless crystals, m.p. 243–245°, $[\alpha]_D$ +81·5° (*c*. 0·825 in dioxan) (Found: C, 61·68, 61·88; H, 5·59, 5·62. Calc. for $C_{15}H_{16}O_6$: C, 61·64; H, 5·52%). Literature[7] gives m.p. 240–244°, $[\alpha]_D$ +91·1° (*c*. 0·472 in dioxan). The i.r. spectrum of dihydromikanolide was identical with that of an authentic specimen.

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