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ISOLATION OF PETASITENINE, A CARCINOGENIC PYRROLIZIDINE ALKALOID FROM *FARFUGIUM JAPONICUM*

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Farfugium japonicum Kitam. (Compositae) is used in Japan as a medicinal herb and foodstuff, and the carcinogenic activity of this plant has recently been reported (1). Isolation of two alkaloids, senkirkine (2) and farfugine (3), from this plant was previously reported. As part of our continuing studies on carcinogenic compounds in the edible plants, we describe here the isolation of petasitenine, a carcinogenic pyrrolizidine alkaloid from *F. japonicum*. Petasitenine was previously isolated from *Petasites japonicus* Maxim. (4,5) and proved to be the carcinogenic principle of this plant (6). The result of the present study provides the first example of the isolation of petasitenine from a plant other than *P. japonicus*.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Spectra were recorded on the following instruments: ir, JASCO Model IRS; ¹H nmr, JEOL JNM-FX90QE; ms, Hitachi RMU-6C. Optical rotation was measured with a JASCO DIP-181 digital polarimeter. Adsorbents for cc and preparative tlc were Aluminiumoxid 90 (Activity II-III) and Alumina 150 F₂₅₄ Type T obtained from E. Merck.

PLANT MATERIAL.—Plants of *F. japonicum* were collected in Nagoya, Japan in June 1980 and were identified by a botanist, H. Wakita. A voucher specimen (no. HN-FJK-1) is deposited at the Herbarium of the Laboratory of Organic Chemistry, Faculty of Science, Nagoya University.

EXTRACTION AND ISOLATION OF PETASITENINE.—The dried and pulverized plant materials (400 g) were extracted with EtOH (4 liters) for 20 days at room temperature. The EtOH extracts, after concentration, gave a residue, which was diluted with H₂O (50 ml). The mixture was acidified (pH 2) with 0.5M H₂SO₄ and extracted with Et₂O (4×200 ml). The aqueous phase was made basic (pH 10) with NH₄OH and extracted with CHCl₃ (4×300 ml). Concentration of the CHCl₃ extracts gave an alkaloidal mixture (147 mg), which was chromatographed on alumina (10 g) with CHCl₃-MeOH (100:1) to afford a fraction (80 mg) containing petasitenine and senkirkine. Further separation and purification by preparative tlc on alumina with CHCl₃-MeOH (100:1) gave petasitenine (5.4 mg, 0.001%), mp 127-128°, [α]²³_D +51° (c=1.00, EtOH) and senkirkine (23.9 mg, 0.006%). Identification of petasitenine and senkirkine was performed by comparison of the spectral (ir, ¹H nmr, and ms) data with those of the authentic specimens, respectively.

Full details of the isolation and identification of petasitenine are available on request to the senior author.

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FLAVONOIDS FROM THE ROOTS OF *TEPHROSIA ELATA*

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Tephrosia elata Deflers (Leguminosae) is a short-lived, bushy perennial that occurs in Kenya on grassland, formerly cultivated land, and thicket margins in the highlands up to 6000 ft. (1). From a study of the seeds of *T. elata*, we have recently reported the isolation of isopongaflavone and tephrosin as feeding deterrents for *Spodoptera exempta*, *Eldana saccharina*, and *Maruca testulalis* larvae, and the identification of certain members of a community of insects associated with the seed pods of *T. elata* (2). Here we report the isolation and identification of six flavonoids from the roots of *T. elata*. They have been identified as the flavanones 8-(3,3-dimethylallyl)-5,7-dimethoxyflavanone and obovatin methyl ether, the flavone warangalone (scandeneone), the pterocarpan (+)-pisatin and (-)-maackiain, and the rotenoid tephrosin. Although isopongaflavone was found to occur in large quantities (1.2%) in the seeds of *T. elata* (2), we were unable to detect it in the roots.

8-(3,3-Dimethylallyl)-5,7-dimethoxyflavanone has previously been isolated from *Lonchocarpus costaricensis* (3) while obovatin methyl ether has been isolated from *Tephrosia obovata* (4), *Tephrosia praecans* (5), and *L. costaricensis* (3). Warangalone has been isolated from *Derris scandens* (6). (+)-Pisatin is a major phytoalexin of *Pisum sativum* (7), while (-)-maackiain has been isolated as a phytoalexin from several species of Leguminosae (8).

The isolation of pisatin and maackiain from apparently healthy roots of *T. elata* is interesting. Except for hildecarpin, an insect antifeedant 6a-hydroxypterocarpan that we recently isolated from *Tephrosia hildebrandtii* Vatke (9), pterocarpan has been isolated from *Tephrosia* only as phytoalexins, the formation of which has been induced by inoculation of the plants with microorganisms (10).

EXPERIMENTAL

PLANT MATERIAL.—The roots of *T. elata* were collected in March 1983, near Thika, Kenya. A voucher specimen (No. 2357) is deposited in the Department of Botany Herbarium, University of Nairobi, Nairobi, Kenya.

EXTRACTION, ISOLATION AND IDENTIFICATION.—The air-dried roots (1.25 kg) were ground and extracted with MeOH in the cold, and the extract was evaporated in vacuo to give a gummy residue (76.0 g). A portion of this residue (33.0 g) was partitioned between H₂O and CHCl₃ and the latter fraction evaporated in vacuo to yield an oil (22.1 g). The oil was purified by column chromatography using silica gel and a CHCl₃/EtOAc gradient (2-100%) as the eluent. Further purification of the fractions from the column by column and preparative tlc on silica gel using a toluene/EtOAc gradient (2-50%) and toluene-hexane-EtOAc (3:4:3 v/v), respectively, as eluents afforded 8-(3,3-dimethylallyl)-5,7-dimethoxyflavanone (46 mg), obovatin methyl ether (71 mg), warangalone (scandeneone) (8 mg), (+)-pisatin (7 mg), (-)-maackiain (7 mg), and tephrosin (101 mg). The identification of the flavonoids was based on comparison of spectroscopic data (¹H and ¹³C nmr, ms, ir, uv) with literature values.

Full details of the isolation and identification of the compounds are available on request from the senior author.