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MAXIMA ISOFLAVONE J: A NEW *O*-PRENYLATED ISOFLAVONE FROM *TEPHROSIA MAXIMA*

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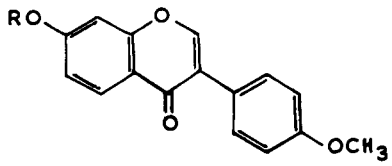
Our phytochemical and pharmacological screening of Indian *Tephrosia* species resulted in the isolation and characterization of several new flavonoids (1-5). In continuation of our study on the isoflavones of *Tephrosia maxima* Pers. (Leguminosae) (3-5), we wish to report here, in addition to calpogonium isoflavone B, the isolation and structure of a new *O*-prenylated isoflavone named maxima isoflavone J. The plant is used as a fish poison and insecticide (6).

Column chromatography of the root petrol extract of *T. maxima* yielded an isoflavone mixture which, on repeated preparative tlc, yielded a yellow fluorescent compound. This was identified as calpogonium isoflavone B (7) by mmp, co-tlc, and spectral data.

Column chromatography of the $CHCl_3$ extract of the root yielded a crystalline isoflavone fraction that gave a single spot on tlc. Cims of the fraction gave three ions *m/z* 337 (100), 311 (75.3), and 269 (40.7). The ^{1}H-nmr spectrum showed the presence of maxima isoflavone A (3) along with another isoflavone having a γ,γ-dimethylallyloxy group (see Experimental section) and one methoxy group as substituents. Since the two compounds could not be separated by column or preparative tlc, it was necessary to treat the mixture with diluted HCl and separate the products by column chromatography. The unchanged maxima isoflavone A was eluted first and identified by mp, co-tlc, and spectral data.

The later fractions gave a phenolic isoflavone (formed from the isoflavone having a γ,γ-dimethylallyloxy group), which gave a negative Labat test and formed a monoacetate. In the ^{1}H-nmr spectrum of the acetate, the downfield singlet at δ 7.98 clearly indicated the isoflavone nature of the compound (8). The ^{1}H nmr also showed the presence of methoxy and acetoxy groups at the 7 and 4′ positions of the isoflavone nucleus. The relative positions of the methoxy and hydroxy substituents in the phenolic isoflavone were determined as 4′ and 7, respectively, by the ms which showed the expected fragmentation pattern (9). The hydroxyl group at 7 was also indicated by the uv data. Thus, the phenolic isoflavone corresponded with formononetin (**1**) (10). Thereby, the structure of maxima isoflavone J was deduced as 7-γ,γ-dimethylallyloxy-4′-methoxy flavone (**2**) or the γ,γ-dimethyallyl ether of formononetin (**1**).



1 R=H
2 R=$-CH_2-CH=C(CH_3)_2$

EXPERIMENTAL

PLANT MATERIAL.—The plant material was collected during October 1982, on and near the Andhra University Campus, Waltair. The plants were identified as *Tephrosia maxima* Pers. (Leguminosae) by Prof. R.S. Rao and Dr. S. Sudhakar, and a voucher specimen is kept in the herbarium of the Department of Botany, Andhra University, Waltair.

EXTRACTION AND ISOLATION.—The powdered root (2.2 kg) was extracted repeatedly and successively with petrol and $CHCl_3$. Both extracts (23 g, 29 g, respectively) were chromatographed over a silica gel column (Acme, silica gel finer than 200 mesh) using solvents or solvent mixtures of increasing polarity as eluents. The fractions were analyzed by tlc (Acme, Silica gel G for tlc) with the solvent system C_6H_6-Me_2CO

(98:2). The isoflavones were detected by uv light and by spraying with 10% alcoholic H_2SO_4.

ISOLATION OF CALPAGONIUM ISOFLAVONE B.—C_6H_6 eluates of the petrol extract chromatogram, after purification by preparative tlc, crystallized from $CHCl_3$-MeOH to give calpogonium isoflavone B (45 mg), mp 164-165°, which showed a green color in the Labat test; this compound was identical by direct comparison (mp, uv, ir, ^1H nmr, ms) with an authentic sample (7).

ISOLATION OF ISOFLAVONE MIXTURE.—The $CHCl_3$ extract when chromatographed and eluted with 0.5% MeOH in $CHCl_3$ gave an isoflavone mixure (160 mg) as needles from $CHCl_3$-MeOH, mp 181-185°. The ^1H-nmr spectrum (90 MHz, $CDCl_3$) showed characteristic signals at δ 1.77 [*s*, $=C(CH_3)_2$], 3.8 (*s*, $-OCH_3$), 4.57 (*d*, $-OCH_2-$), 5.45 (*t*, =CH), 5.92, 6.13 (2*s*, $-OCH_2O-$). Eims, 70 eV, showed fragments at *m/z* 337 (10.7), 336 (5.8), 311 (16.4), 310 (24.0), 269 (47), 268 (8.7), 253 (9.1), 164 (21.2), 146 (17.2), 136 (11.5), and 132 (17.8). Cims (CH_4) showed fragments at *m/z* 338 (21), 337 (100), 311 (80.1), and 269 (60.7).

ACID TREATMENT OF THE ISOFLAVONE MIXTURE AND ISOLATION OF FORMONONETIN (**1**).—The isoflavone mixture (150 mg) was treated with 2 N alcoholic HCl (30 ml) and refluxed for 3 h. The alcoholic solution was evaporated to half the volume, and the product obtained after keeping overnight was filtered and dried. It was then separated by column chromatography over silica gel. The 2% MeOH in $CHCl_3$ eluates showed a single spot on silica gel tlc (2% MeOH in $CHCl_3$) and crystallized to give formononetin (**1**) (65 mg) as needles from EtOH, mp 258°, identified by uv, ir, ^1H nmr, and ms (10), preparation of the acetate, mp 170-171°, and identification by ^1H nmr (11).

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