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FLAVANONES FROM *TEPHROSIA LEIOCARPA*

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Key Word Index—*Tephrosia leiocarpa*; Leguminosae; prenyl flavanones; tephroleocarpin A and B.

Abstract—Roots and aereal parts of *Tephrosia leiocarpa* afforded two new flavanones, 5-hydroxy-7-methoxy-8-(3-hydroxy-3-methyl-*trans*-but-1-enyl)flavanone and 5-hydroxy-7-methoxy-8-(3-methyl-*trans*-but-1,3-dienyl)flavanone, named tephroleocarpin A and B, respectively.

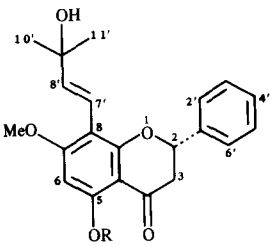
INTRODUCTION

Chemical investigation on *Tephrosia* species have yielded rotenoids and other flavonoids of chemotaxonomic importance in the genus [1]. As part of our chemical systematic study of the genus *Tephrosia*, we have previously investigated several Mexican species and isolated a number of a new flavonoids [2–7]. We now describe a study of *Tephrosia leiocarpa*, an endemic species from the western part of México. The results follow the expected chemotaxonomic pattern of the genus.

RESULTS AND DISCUSSION

The extracts of roots and aerial parts of *Tephrosia leiocarpa* afforded after CC and preparative TLC over silica gel, two new flavanones, tephroleocarpin A (**1**) and B (**2**), in addition to the known terpenoids: geijerene and 1,5-dimethyl-1,5,7-cyclodecatriene; a mixture of sterols: sitosterol and stigmasterol; the rotenoids: rotenone, rotenolone B, dehydrorotenone and tephrosin as well as the known flavanones 7-methylglabranin and obovatin. Identification of known compounds was based on comparison with authentic samples and published data.

Tephroleocarpin A (**1**) is a yellowish crystalline compound, mp 99–101°. Its M_r as determined by mass spectrometry was in accord with the molecular formula $C_{21}H_{22}O_5$. Both the IR (3580, 1635, 1580 cm^{-1}) and the UV (206, 262, 356 nm) absorptions suggested a hydroxyflavanone structure [8]. The ^1H NMR spectrum confirmed the above suggestion, since it showed the characteristic ABX system signals of the flavanone nucleus at δ5.40 (H-2) and 2.95 (H-3). The rest of the spectrum (Table 1), was similar to that of quercetol C (**3**), previously isolated from *Tephrosia quercetorum* [7], except that one methoxyl signal was missing and instead it showed a chelated hydroxyl signal at δ12.85; therefore, the hydroxyl group must be at C-5 and the methoxyl group at C-7. The EI mass spectrum showed a molecular ion peak at *m/z* 354, together with other fragment peaks at *m/z* 339 $[M-Me]^+$, 336 $[M-H_2O]^+$, 193 $[C_{10}H_9O_4]^+$ and 77 which are consistent with the structure **1**. The negative value of the optical rotation $[\alpha]_D$ −62.13° indicated the absolute configuration *S* at C-2 in tephroleocarpin A (**1**) [8]. These results indicate that tephroleocarpin A (**1**) must be 5-*O*-demethylquercetol C. Confirmation of the structure was achieved by methylation of **1** with methyl iodide. This gave the methyl ether **3** which was identical in all respects with quercetol C [7].



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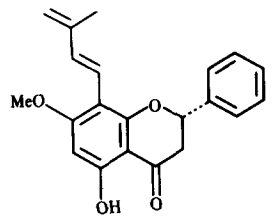

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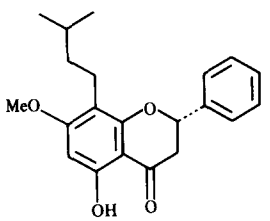

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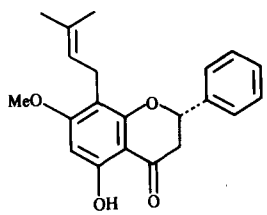

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Tephroleocarpin B (**2**), $C_{21}H_{26}O_4$, ($[M]^+$ 342), was a yellow amorphous solid, mp 265–270°, $[\alpha]_D$ −92.55 ($CHCl_3$). The UV (203, 288, 340 nm) and the IR (3440, 1635, 1575, 880 cm^{-1}) spectra were similar to those of **1** and typical of flavanones [8]. Again, the structure of **2** followed from the ^1H NMR spectral data (Table 1) which

*Part 7 in the series 'Flavonoids from *Tephrosia* species'. For part 6 see ref. [7].

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Table 1. ^{1}H NMR spectral data of flavonoids **1**, **2** and **4** (ppm (δ), 80 MHz, $CDCl_3$, TMS as int. standard)

H	1	2	4
2	5.35 *dd* (4, 12)	5.40 *dd* (4, 10)	5.40 *dd* (4, 12)
3	2.95 *m*	2.95 *m*	2.95 *m*
6	6.08 *s*	6.10 *s*	6.05 *s*
$-\phi$	7.39 *s*	7.40 *s*	7.40 *s*
7′	6.75 *d* (8)	7.19 *d* (17)	2.55 *m*
8′	6.55 *d* (8)	6.62 *d* (17)	1.35 *m*
10′	1.35 *s*	4.90 *s*	0.85 *d* (7)
11′	1.35 *s*	1.90 *s*	0.85 *d* (7)
−OMe	3.85 *s*	3.90 *s*	3.85 *s*
−OH	12.85 *s*	12.25 *s*	12.11 *s*

Values in parentheses are coupling constants or line separations in Hz.

showed that **2** must have the same substitution as **1** but a different side chain at C-8. While tephroleocarpin A (**1**) has a 3-hydroxy-3-methyl-*trans*-but-1-enyl side chain, tephroleocarpin B (**2**) has a 3-methyl-*trans*-but-1,3-dienyl as indicated by two singlets at δ1.90 (3H) and 4.90 (2H) and two doublets (J = 17.0 Hz) at δ7.19 (1H) and 6.62 (1H) typical for this group in the ^{1}H NMR spectrum [10]. The mass spectrum showed a $[M]^+$ at *m/z* 336 and other significant fragments at *m/z* 321 $[M-Me]^+$, 217 $[C_{12}H_9O_4]^+$, 189 $[C_{11}H_9O_9]^+$, 104, 91 and 77 consistent with the proposed structure for tephroleocarpin B (**2**). Catalytic hydrogenation of **2** gave the corresponding tetrahydro derivative **4** ($[M]^+$ 340), mp 109–110°. The ^{1}H NMR spectrum of **4** (Table 1) clearly showed a two-methyl doublet at δ0.85 (J = 7.0 Hz). The mass spectrum showed a $[M]^+$ at *m/z* 340 among other peaks at *m/z* 283 $[M-C_4H_9]^+$, 179 $[A-C_4H_9]^+$, 104 $[C_8H_8]^+$, and 77 according with structure **4**. Final confirmation of the structure **2** was achieved by dehydration of tephroleocarpin A (**1**) which furnished tephroleocarpin B (**2**), as well as by catalytic hydrogenation of 5-hydroxy-7-methoxy-8-prenylflavanone (**5**) which gave a dihydro derivative, identical in all respects with the tetrahydro derivative **4** obtained by hydrogenation of **2**. Most likely **1** is the precursor of **2**, which might be an artifact formed by dehydration of **1**.

EXPERIMENTAL

Tephrosia leiocarpa was collected in August 1983, at the Estación Experimental de Biología 'Chamela', el Arroyo, Jalisco, México, 1983. A voucher is on deposit at the Herbarium of Instituto de Biología (UNAM). Air-dried leaves and flowers (1.06 kg) were extracted successively with petrol, EtOAc and MeOH. After evapn of solvents the green syrups A (25.3 g), B (43.0 g) and C (67.0 g) were obtained. In the same way from the air-dried roots (485 g) thick yellow extracts D (5.4 g), E (15.0 g) and F (23.5 g) were obtained.

The petrol extract A afforded after CC, a mixture of ubiquitous sterols, sitosterol and stigmasterol. The EtOAc extract B, was fractionated over silica gel (450 g) using petrol and CH_2Cl_2. The petrol fractions were combined (8.2 g) and chromatographed on silica gel (90 g) using petrol and mixtures of petrol–CH_2Cl_2 of increasing polarity as eluants. Frs 12–17 (306 mg) eluted with petrol–CH_2Cl_2 (4:1) after further purification by prep. TLC gave 20 mg of a mixture of rotenolone B and tephrosin [9]. Frs 18–26 (25 mg) eluted with petrol–CH_2Cl_2 (3:1) provided 18 mg of dehydrorotenone, mp 210–215° (lit. 218° [11]).

The petrol extract D was chromatographed over silica gel (60 g) using petrol and mixtures of petrol–CH_2Cl_2. Frs 1–2 (520 mg) were sepd by prep. GC to give 8 mg geijerene and 4 mg 1,5-dimethyl-1,5,7-cyclodecatriene [12]. Rechromatography of frs 9–43 over silica gel (30 g) provided 765 mg of 7-methylglabranin (5-hydroxy-7-methoxy-8-prenylflavanone), 572 mg of obovatin [13] and 87 mg of a mixture of sitosterol and stigmasterol. From the EtOAc extract E, frs eluted with petrol afforded further amounts of 7-methylglabranin (926 mg) and frs eluted with petrol–CH_2Cl_2 (8:1) afforded 47 mg of 5-hydroxy-7-methoxy-8-(3-hydroxy-3-methyl-*trans*-but-1-enyl)flavanone (tephroleocarpin A) (**1**). Frs eluted with petrol–CH_2Cl_2 (7:2 and 2:1) after purification by prep. TLC provided 6 mg of rotenone and 22 mg of 5-hydroxy-7-methoxy-8-(3-methyl-*trans*-but-1,3-dienyl) flavanone (tephroleocarpin B) (**2**).

Tephroleocarpin A (**1**). $C_{21}H_{22}O_5$, yellowish crystals, mp 99–101°, $[\alpha]_D$ −62.13° ($CHCl_3$; *c* 0.103); UV λ_{max}^{MeOH} nm (ε): 206 (23 958), 262 (31 354), 356 (3129); EIMS (probe) 70 eV *m/z* (rel. int.): 354 [M, $C_{21}H_{22}O_5]^+$ (42.0), 339 $[M-Me]^+$ (54.0), 336 $[M-H_2O]^+$ (31.0), 321 $[M-Me-H_2O]^+$ (32.0), 283 $[M-C_4H_7]^+$ (95.0), 193 $[C_{10}H_9O_4]^+$ (100.0), 77 (21.0).

Tephroleocarpin B (**2**). $C_{21}H_{20}O_4$, amorphous solid, mp 265–270°, $[\alpha]_D$ −92.5° ($CHCl_3$; *c* 0.094); UV λ_{max}^{MeOH} nm (ε): 203 (18 327), 288 (8560), 340 (1863); EIMS (probe) 70 eV *m/z* (rel. int.): 336 [M, $C_{21}H_{20}O_4]^+$ (100.0), 321 $[M-Me]^+$ (33.0), 217 $[C_{12}H_9O_4]^+$ (60.0), 189 $[C_{11}H_9O_3]^+$ (34.0), 104 (18.0), 91 (23.0), 77 (50.0).

Methylation by MeI–K_2CO_3–Me_2CO of tephroleocarpin A (**1**) afforded **3** (10 mg), mp 198–200° (ref. [7] 198–200°), identified by comparison with an authentic sample. Dehydration of tephroleocarpin A (**1**): dry $MgSO_4$ (100 mg) was added to a soln of **1** in C_6H_6 and refluxed for 20 min, the reaction being monitored by TLC. When the reaction was completed the $MgSO_4$ was filtered and the solvent evapd yielding 9 mg of tephroleocarpin B (**2**). Hydrogenation of tephroleocarpin B (**2**): catalytic hydrogenation of **2** (15 mg) in MeOH using PtO_2 as catalyst gave, after TLC purification, 10 mg of the tetrahydro derivative **4**, mp 109–110°, $[\alpha]_D$ −82.75° ($CHCl_3$, *c* 0.174), UV $\lambda_{max}^{CHCl_3}$ nm (ε): 210 (28 701), 290 (17 105), 337 (3696); EIMS (probe) 70 eV *m/z* (rel. int.): 340 $[M]^+$ (28), 283 $[M-C_4H_9]^+$ (99), 179 $[C_9H_7O_4]^+$ (100), 104 $[C_8H_8]^+$ (77), 77 $[C_6H_5]^+$ (7). Hydrogenation of 7-methyl-glabranin (**5**): catalytic hydrogenation of **5** (20 mg) in MeOH using PtO_2 as catalyst gave, after TLC purification, 14 mg of a crystalline compound which was identical to **4** in all respects.

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A CHROMENOFLAVANONE AND TWO CAFFEIC ESTERS FROM *PONGAMIA GLABRA*

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Key Word Index—*Pongamia glabra*; Leguminosae; stem bark; flavonoids; (−)-isoglabrachromene; hexacosanyl caffeate; triacontanyl caffeate; betulinic acid.

Abstract—(−)-Isoglabrachromene, a new natural chromenoflavanone, and hexacosanyl caffeate and triacontanyl caffeate, two new esters, have been isolated together with 11 known flavonoids and betulinic acid from the stem bark of *Pongamia glabra*. The reason why the H-α and H-β of 2′-hydroxy-6′-methoxychalcones appear at the same field in their ^{1}H NMR spectra is discussed.

INTRODUCTION

All parts of *Pongamia glabra* Vent. (Leguminosae) have been extensively studied. Furano-, chromeno- and simple flavonoids have been found to be the major chemical constituents of this plant. Our previous investigation on the flowers resulted in the isolation of three new hydroxyfuranoflavones [1, 2]. Subsequent work by other groups on different parts of this plant has resulted in several new flavonoids. The occurrence of several triterpenoids in the leaves has also been reported [3]. The stem bark and roots of this plant have not been investigated in recent years. We, therefore, undertook a reinvestigation of the stem bark of *P. glabra*.

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RESULTS AND DISCUSSION

Extensive chromatography of the concentrate of the cold extract of the stem bark of *P. glabra* over silica gel afforded a new natural chromenoflavanone (−)-isoglabrachromene (**1**), two new caffeic esters, hexacosanyl caffeate (**2a**) and triacontanyl caffeate (**2b**) (isolated as a mixture), the known flavonoids glabrachromene (**3**), ovalitenone, pongachromene, 5-methoxy-3′,4′-methylenedioxy-2″,2″-dimethylpyrano(7,8-6″,5″)flavone, lanceolatin B, karanjin, pongapin, glabra-II, kanugin, desmethoxykanugin and fisetin tetramethyl ether and the triterpene betulinic acid.

(±)-Isoglabrachromene (**1**) was previously known as the cyclization product of the natural chalcone glabrachromene (**3**) [4]. Subrahmanyam *et al.* [4] carried out the cyclization with TLC grade silica gel (prolonged treatment) and Malik *et al.* [5] with methanolic sodium acetate. In this study (−)-**1**, mp 167–168°, $[\alpha]_D^{25}$ −69.4°