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Phenolic compounds from *Pterocaulon alopecuroides*

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1. Subject and source

Aerial parts of *Pterocaulon alopecuroides* (Lam.) DC. (Asteraceae), were collected at the flowering stage in December 2003 in Salta, Argentina. The identification was carried out by Ing. Julio Tolaba. A voucher specimen (n° 3399) is on deposit at the Museo de la Facultad de Ciencias Naturales, Universidad Nacional de Salta, Salta, Argentina.

2. Previous work

Previous phytochemical studies of aerial parts of *P. alopecuroides* collected in Brazil revealed the presence of coumarins (Stein et al., 2007; Vilegas et al., 1995) and one dihydroflavonol (Vilegas et al., 1995). Recently, we reported the isolation of six flavonoids from *P. alopecuroides* and their antibacterial activity (Alarcón et al., 2008).

3. Present study

In continuation of our earlier investigation (Alarcón et al., 2008), we now report on the isolation and structure elucidation of the new flavonoids **1a**/**1b**, **2a**/**2b** and **3**, one new coumarin **4**, and the known compounds, dihydrokaempferol **5** and 7-(2,3-dihydroxy-3-methylbutoxy)-6-methoxycoumarin **6**.

Air-dried aerial parts (300 g) of *P. alopecuroides* were macerated in EtOH for 7 days at room temperature. The organic solution was distilled under reduced pressure at 40 °C to obtain 70.0 g of crude extract. This extract was suspended in H_2O (500 mL) and then extracted with CH_2Cl_2 (4 × 200 mL).

The CH_2Cl_2 soluble extract (20.0 g) was divided into 2 fractions by flash column chromatography on silica gel C-18 (70 g) (7 × 15 cm), eluting with MeOH:H_2O (9:1, 500 mL) and MeOH (500 mL). The first fraction (6.5 g) was subjected to VLC using

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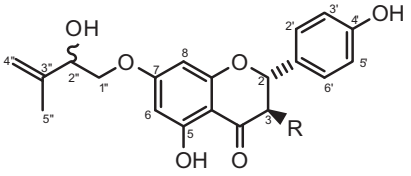
a Büchner type funnel with fibrous glass frit (disc diam. 150 mm, capacity 400 mL) filled with 250 g of silica gel, each subfraction (250 mL) was eluted with hexane (F_1), hexane–EtOAc 7:3 (F_2), hexane–EtOAc 1:1 (F_3), hexane–EtOAc 3:7 (F_4), EtOAc (F_5).

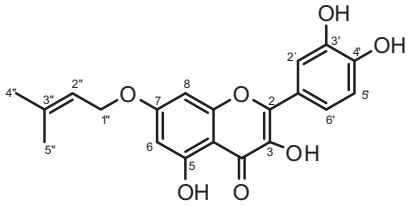
F_2 (107 mg) was chromatographed on a silica gel column (2 × 30 cm, 40 g) using hexane containing increasing amounts Et_2O (0–100%); a total of 100 fractions (10 mL each) were collected. The fractions 81–85 (15 mg, hexane–Et_2O 2:8), were purified by preparative TLC (hexane–EtOAc 7:3, runs × 3) to give compounds **1a**/**1b** as a pair of inseparable epimers (2.5 mg, $R_f = 0.30$).

F_3 (780 mg) was first purified by CC on silica gel (3 × 30 cm, 60 g) eluting with CH_2Cl_2 (200 mL), CH_2Cl_2–Me_2CO 9.5:0.5 (200 mL), CH_2Cl_2–Me_2CO 9:1 (200 mL) and CH_2Cl_2–Me_2CO 8:2 (200 mL); fractions of 10 mL were collected. The fractions eluted with CH_2Cl_2–Me_2CO (9.5:0.5) were chromatographed on a 230–400 mesh silica gel column eluting with a gradient of *n*-hexane–Et_2O to yield 7.0 mg of **4**.

F_4 (1.11 g) was first chromatographed on a silica gel column (4 × 30 cm, 90 g) eluted with mixtures of CH_2Cl_2–Me_2CO of increasing polarities (1%) from 100:0 to 80:20 (200 mL, each). Fraction eluted with CH_2Cl_2–Me_2CO (8.5:1.5) was purified on preparative RPTLC (MeOH–H_2O 3:2, runs × 2) to afford 4.0 mg of **3** ($R_f = 0.11$). The fraction eluted with CH_2Cl_2–Me_2CO (8:2) was purified on preparative RPTLC (MeOH–H_2O 3:2) to give compounds **2a**/**2b** (6.0 mg, $R_f = 0.42$) as a pair of inseparable epimers, and **5** (4.7 mg, $R_f = 0.62$).

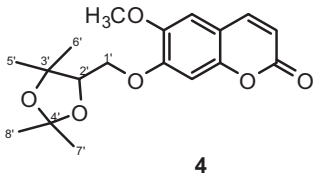
F_5 (1.41 g) was subjected to silica gel column chromatography with a gradient of *n*-hexane–EtOAc to give 100 mg of **6**.



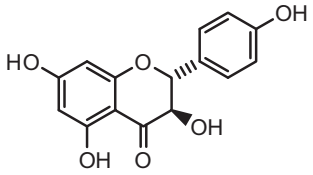


3

	R
1	H
2	OH



4



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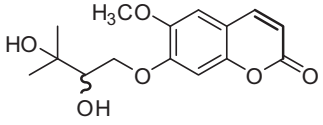

6

The compounds were identified by spectroscopic methods (UV, IR, ^1H and ^{13}C NMR, HR-ESI-MS). The NMR spectra were recorded on a Bruker Avance 400 (^1H at 400 MHz and ^{13}C at 100 MHz) spectrometer with TMS as internal reference. HRMS were performed on a Bruker micrOTOF-QII spectrometer. IR spectra were taken on an IR-FT Bruker model IFS-88 spectrometer. UV spectra were recorded on a Shimadzu UV-260 instrument. CD spectra were obtained on a Jasco 810 spectropolarimeter.

Dihydrokaempferol **5** (Markham and Geiger, 1994) and 7-(2,3-dihydroxy-3-methylbutiloxy)-6-methoxycoumarin **6** (Vilegas et al., 1995; Debenedetti et al., 1998) were identified by comparison of their spectral properties with those reported in literature. The structure of the compounds **1a**/**1b**, **2a**/**2b**, **3** and **4** was established on the basis of 1D NMR (^1H NMR, ^{13}C NMR), 2D NMR (^1H–^1H COSY, HSQC, HMBC), and HR-ESI-MS.

Compounds **1a**/**1b** were isolated as amorphous solids, and the molecular formula was determined to be $C_{20}H_{20}O_6$ from analysis of its HR-ESI-MS and NMR spectroscopic data. Its UV spectrum displayed absorption bands at 295 and 335 (sh) nm. The ^1H and ^{13}C NMR spectra of **1a**/**1b** (Table 1, $CDCl_3$) were consistent with a flavanone skeleton (Mabry et al., 1970). The ^1H NMR spectrum also exhibited resonances for a 1,4-disubstituted benzene unit (H-2′, H-3′, H-5′ and H-6′), a set of meta-coupled

Table 1
^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) data and long-range HMBC correlations for **1a**/**1b** ($CDCl_3$).

Position	**1a**		**1b**		HMBC (^{1}H → ^{13}C)
	δ ^{13}C	δ ^{1}H	δ ^{13}C	δ ^{1}H	
2	79.0	5.36 dd (3.0; 13.0)	79.1	5.39 dd (3.0; 13.0)	C-3, C-4
3	42.8	3.10 dd (13.0, 17.3)	43.0	3.10 dd (13.0, 17.3)	C-2, C-4
		2.80 dd (3.0; 17.3)		2.80 dd (3.0; 17.3)	
4	195.9	–	195.9	–	–
5	164.1	–	164.1	–	–
6	95.7	6.09 d (2.2)	95.7	6.09 d (2.2)	C-5, C-7, C-8
7	168.0	–	168.0	–	–
8	94.7	6.06 d (2.2)	94.7	6.06 d (2.2)	C-7, C-9, C-10
9	162.9	–	162.9	–	–
10	103.2	–	103.2	–	–
1′	129.5	–	129.5	–	–
2′	127.8	7.33 d (8.0)	127.8	7.33 d (8.0)	C-1′, C-4′
3′	115.6	6.88 d (8.0)	115.6	6.88 d (8.0)	C-4′
4′	156.2	–	156.2	–	–
5′	115.6	6.88 d (8.0)	115.6	6.88 d (8.0)	C-4′
6′	127.8	7.33 d (8.0)	127.8	7.33 d (8.0)	C-1′, C-4′
1″	71.4	4.07 dd (3.0; 9.0)	72.5	4.10 dd (3.0; 9.0)	C-2″, C-3″, C-7
		3.95 dd (8.0; 9.0)		3.98 dd (8.0; 9.0)	
2″	73.1	4.49 dd (3.0; 8.0)	74.2	4.47 dd (3.0; 8.0)	C-1″, C-4″, C-3″
3″	145.0	–	145.0	–	–
4″	113.1	5.15 s	114.7	5.12 s	C-3″, C-2″
		5.04 s		5.02 s	
5″	18.9	1.60 s, br	18.9	1.60 s, br	C-4″
5-OH	–	12.00 s	–	12.00 s	C-5, C-6, C-10

Coupling constant values (in parentheses) are in Hz.

aromatic protons (H-6 and H-8), a chelated phenolic group (5-OH), and a 2-hydroxy-3-methyl-3-butenyloxy group. A chiral centre existing in the 2-hydroxy-3-methyl-3-butenyloxy group of **1a**/**1b** resulted in the occurrence of epimers and slightly different resonances of these unresolved epimers were observed in the ^{1}H and ^{13}C NMR spectra of **1a**/**1b** (Table 1). The attachment of the 2-hydroxy-3-methyl-3-butenyloxy moiety was determined to be at C-7 by the detection of HMBC correlations from H-1″ to C-2″, C-3″ and C-7. HMBC correlations between a quaternary carbon at δ 156.2 and H-2′, H-3′, H-5′ and H-6′ indicated 4′-hydroxy substitution. The stereochemistry at C-2 was determined to be *S* by analysis of the CD spectrum, in which a positive Cotton effect was observed at 328 nm along with negative Cotton effect at 288 nm (Slade et al., 2005). Thus on the basis of above spectral studies the structures of epimers **1a**/**1b** were elucidated as (2*S*)-5,4′-dihydroxy-7-(2-hydroxy-3-methyl-3-butenyloxy)flavanone.

The molecular formula of the compounds **2a**/**2b** was established by HR-ESI-MS as $C_{20}H_{20}O_7$. Its UV spectrum displayed absorption bands at 290 and 330 (sh) nm. The ^{1}H and ^{13}C NMR spectra (Table 2, Me_2CO-d_6) exhibited typical signals of 2,3-trans-dihydroflavonol-type skeletons (Clark-Lewis, 1968; Harborne and Mabry, 1982). The region of aromatic protons in the ^{1}H NMR spectrum is similar to that of **1a**/**1b**. This spectrum further showed the presence of a chelated hydroxy group (5-OH) and signals due to a 2-hydroxy-3-methyl-3-butenyloxy group. The ^{1}H NMR and ^{13}C NMR spectra of **2a**/**2b** (Table 2), showed that this compound was recovered as a mixture of epimers at the asymmetric centre of the 2-hydroxy-3-methyl-3-butenyloxy group. The positions of the 2-hydroxy-3-methyl-3-butenyloxy substituent at C-7 and the hydroxyl group at C-4′ were established by 2D NMR ^{1}H-^{13}C HMBC experiments (Table 2). A 2*R*, 3*R*-configuration was assigned to compounds **2a**/**b** by analysis of the CD spectrum, in which a positive Cotton effect was observed at 329 nm (Slade et al., 2005). Consequently, the structure of compounds **2a**/**2b** was established as (2*R*, 3*R*)-5,4′-dihydroxy-7-(2-hydroxy-3-methyl-3-butenyloxy)dihydroflavonol.

Compound **3** was obtained as a yellow amorphous solid. The molecular formula was determined as $C_{20}H_{18}O_7$ by the HR-ESI-MS. The UV spectrum of **3** showed an absorption maxima at 260 (Band II) and 370 (Band I) nm in MeOH, and bathochromic shifts of 15 nm with $AcONa/H_3BO_3$ in Band I, indicating that **3** was a flavonol with ortho-dihydroxyl groups in ring B (Mabry et al., 1970). The ^{1}H NMR spectrum (Table 3, Me_2CO-d_6) of **3** showed signals for a chelated hydroxy group (5-OH), two meta-coupled aromatic protons in ring A (H-6 and H-8), a γ,γ-dimethylallyloxy group, and resonances for an ABX system in ring B (H-2′, H-5′ and H-6′) . The complete assignment of all protons and carbons was established by extensive use and interpretation of ^{1}H–^{1}H COSY, HMQC, and HMBC spectra. The γ,γ-dimethylallyloxy group was located at C-7 on the basis of the ^{1}H–^{13}C long-range correlation (Table 3) of the carbon signal at δ 164.0 (C-7) with the proton H-1″. Thus, the structure of **3** was established as 5,3′,4′-trihydroxy-7-(γ,γ-dimethylallyloxy)flavonol.

Compound **4** was obtained as an amorphous solid. Its molecular formula $C_{18}H_{22}O_6$ was deduced from the HR-ESI-MS. The UV spectrum of **4**, displayed absorption bands at 234, 256 (sh) and 320 nm. The ^{1}H NMR spectrum (Table 4, $CDCl_3$) had resonances for protons in the coumarin nucleus corresponding to H-3, H-4, H-5 and H-8. Additional signals in the spectrum were consistent with a (2,2,5,5-tetramethyl-1,3-dioxolan-4-yl)methoxy unit and a methoxyl group. The ^{1}H–^{13}C long-range correlations (Table 4) between H-1′ and C-2′, C-3′ and C-7 proved that a (2,2,5,5-tetramethyl-1,3-dioxolan-4-yl)methoxy unit was linked with C-7, and the correlations between the protons of methoxyl group and C-6 indicated that the methoxyl group

Table 2
^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) data and long-range HMBC correlations for **2a**/**2b** (Me_2CO-d_6).

Position	**2a**		**2b**		HMBC (^{1}H → ^{13}C)
	δ ^{13}C	δ ^{1}H	δ ^{13}C	δ ^{1}H	
2	83.5	5.13 d (11.5)	83.6	5.11 d (11.5)	C-1′, C-2′, C-6′, C-4
3	72.2	4.68 d (11.5)	72.1	4.71 d (11.5)	C-4
4	197.8	–	197.8	–	–
5	163.7	–	163.7	–	–
6	95.5	6.12 d (2.3)	95.5	6.12 d (2.3)	C-5, C-7, C-8, C-10
7	167.6	–	167.8	–	–
8	94.3	6.09 d (2.3)	94.3	6.09 d (2.3)	C-7, C-9, C-6, C-10
9	163.0	–	163.0	–	–
10	101.3	–	101.3	–	–
1′	128.2	–	128.2	–	–
2′	129.5	7.43 d (8.4)	129.5	7.43 d (8.4)	C-2, C-4′
3′	115.0	6.91 d (8.4)	115.0	6.91 d (8.4)	C-1′
4′	157.9	–	157.9	–	–
5′	115.0	6.91 d (8.4)	115.0	6.91 d (8.4)	C-1′
6′	129.5	7.43 d (8.4)	129.5	7.43 d (8.4)	C-2, C-4′
1″	72.4	4.15 dd (3.5; 9.9) 4.01 dd (7.0; 9.9)	72.0	4.12 dd (3.5; 9.9) 4.04 dd (7.0; 9.9)	C-2″, C-7
2″	72.8	4.48 dd (3.5; 7.0)	72.7	4.46 dd (3.5; 7.0)	C-3″
3″	144.8	–	144.7	–	–
4″	111.3	5.11 s, br 4.92 s, br	111.3	5.11 s, br 4.92 s, br	C-3″, C-2″, C-5″
5″	18.1	1.81 s, br	18.1	1.81 s, br	C-4″
5-OH	–	11.70 s	–	11.70 s	C-5, C-6, C-10

Coupling constant values (in parentheses) are in Hz.

was located at C-6. Based on these data, compound **4** was identified as 7-(2,2,5,5-tetramethyl-1,3-dioxolan-4-yl)methoxy-6-methoxycoumarin.

(2S)-5,4′-Dihydroxy-7-(2-hydroxy-3-methyl-3-butenyloxy)flavanone (**1**): Amorphous solid; UV (MeOH) $\lambda_{max} = 285$, 335 (sh); +NaOMe: 360; +NaOAc/H_3BO_3: 285, 330; +$AlCl_3$: 330, 375; +$AlCl_3$/HCl: 330, 375 nm; CD (MeOH, *c* 1.9×10^{-5} M): $\Delta\varepsilon_{288}$ −4.93, $\Delta\varepsilon_{328}$ +1.16; IR (KBr): $\nu_{max} = 3391$, 2919, 2855, 1637, 1573, 1162, 1088 cm^{-1}; for ^{1}H and ^{13}C NMR data, see Table 1; HR-ESI-MS: 357.1253 ($[M + H]^+$); (calc. for $[C_{20}H_{20}O_6 + H]$ 357.1261); EI-MS (70 eV): *m*/*z* = [M$^+$] 356 (7), 273 (69), 272 (42), 153 (100), 152 (43), 120 (62).

(2R,3R)-5,4′-Dihydroxy-7-(2-hydroxy-3-methyl-3-butenyloxy)dihydroflavonol (**2**): Amorphous solid; UV (MeOH) $\lambda_{max} = 290$, 330 (sh); +NaOMe: 290, 355; +NaOAc/H_3BO_3: 290, 335; +$AlCl_3$: 295, 380; +$AlCl_3$/HCl: 295, 380; CD (MeOH, *c* 3.2×10^{-5} M): $\Delta\varepsilon_{329}$ +0.67; IR (KBr): $\nu_{max} = 3415$, 2924, 1640, 1572, 1167, 1088 cm^{-1}; for ^{1}H and ^{13}C NMR data, see Table 1;

Table 3
^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) data and long-range HMBC correlations for **3** (Me_2CO-d_6).

Position	**3**		
	δ ^{13}C	δ ^{1}H	HMBC (^{1}H → ^{13}C)
2	146.4	–	–
3	136.1	–	–
4	175.7	–	–
5	161.0	–	–
6	97.8	6.33 d (2.3)	C-5, C-7, C-8, C-10
7	164.0	–	–
8	92.5	6.71 d (2.3)	C-7, C-9, C-6, C-10
9	156.7	–	–
10	103.9	–	–
1′	122.8	–	–
2′	114.9	7.87 d (2.3)	C-3′, C-4′, C-6′
3′	145.0	–	–
4′	147.6	–	–
5′	115.3	7.02 d (8.5)	C-4′, C-3′, C-1′
6′	120.6	7.73 dd (8.5; 2.3)	C-2′, C-4′
1″	65.4	4.72 d (6.5)	C-2″, C-3″, C-7
2″	119.2	5.52 t, br	C-3″, C-4″
3″	138.2	–	–
4″	25.0	1.82 s, br	C-2″
5″	17.3	1.80 s, br	C-3″, C-2″
5-OH		12.13 s	C-5, C-6, C-10

Coupling constant values (in parentheses) are in Hz.

Table 4
^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) data and long-range HMBC correlations for **4** ($CDCl_3$).

Position	**4**		
	δ ^{13}C	δ ^{1}H	HMBC ($^{1}H \rightarrow {}^{13}C$)
2	161.4	–	–
3	113.6.	6.29 d (9.5)	C-10
4	143.1	7.61 d (9.5)	C-2, C-9
5	108.4	6.87 s	C-4, C-6, C-7, C-10
6	146.7	–	–
7	151.8	–	–
8	101.9	6.90 s	C-6, C-10
9	149.8	–	–
10	112.0	–	–
1′	67.9	4.07 dd (7.0; 3.0)	C-7, C-2′, C-3′
		4.28 m	C-7, C-2′, C-3′
2′	80.4	4.26 m	C-1′
3′	79.9	–	–
4′	108.1	–	–
5′	22.8	1.21 s	C-2′, C-3′, C-6′
6′	26.7	1.43 s	C-2′, C-3′, C-5′
7′	27.0	1.41 s	C-4′, C-8′
8′	28.5	1.46 s	C-4′, C-7′
OCH_3	56.2	3.90 s	C-6

Coupling constant values (in parentheses) are in Hz.

HR-ESI-MS: ($[M+H]^+$) 373.1293; (calc. for $[C_{20}H_{20}O_7+H]$ 373.1282); EI-MS (70 eV): $m/z = [M^+]$ 372 (8), 289 (43), 288 (28), 237 (22), 153 (100), 152 (47), 134 (57), 107 (39).

5,3′,4′-Trihydroxy-7-(γ,γ-dimethylallyloxy)flavonol (**3**): Yellow amorphous solid; UV (MeOH) $\lambda_{max} = 260$, 370; +NaOMe: 270, 425; +NaOAc/H_3BO_3: 260, 300, 385; +$AlCl_3$: 275, 300, 430; +$AlCl_3$/HCl: 275, 300, 430 nm; IR (KBr): $\nu_{max} = 3405$, 2919, 1653, 1590, 1497, 1162, 1092 cm^{-1}; for ^{1}H and ^{13}C NMR data, see Table 2; HR-ESI-MS: 371.1123 ($[M+H]^+$); (calc. for $[C_{20}H_{18}O_7+H]$ 371.1125); EI-MS (70 eV): $m/z = [M^+]$ 370 (19), 302 (100), 301 (96), 137 (34), 109 (18), 69 (73).

7-(2,2,5,5-Tetramethyl-1,3-dioxolan-4-yl)methoxy-6-methoxycoumarin (**4**). White amorphous solid; UV (MeOH) $\lambda_{max} = 234$, 256 (sh), 320 nm; IR (KBr): $\nu_{max} = 3435$, 2929, 1700 (br), 1479, 1331 cm^{-1}; for ^{1}H and ^{13}C NMR data, see Table 3; HR-ESI-MS: 335.1498 ($[M+H]^+$); (calc. for $[C_{20}H_{18}O_7+H]$ 335.1489); EI-MS (70 eV): $m/z = [M^+]$ 334 (2), 236 (68), 177 (4), 78 (55), 57 (100).

Dihydrokaempferol (**5**): White amorphous solid; UV (MeOH) λ_{max}: 290, 335 (sh); +NaOMe: 292, 340; +NaOAc/H_3BO_3: 290, 335; +$AlCl_3$: 315, 380; +$AlCl_3$/HCl: 315, 380. ^{1}H NMR (400 MHz, Me_2CO-d_6): 5.10 (d, $J = 11.6$ Hz, H-2), 4.68 (d, $J = 11.6$ Hz, H-3), 6.01 (d, $J = 2.0$ Hz, H-6), 5.97 (d, $J = 2.0$ Hz, H-8), 7.44 (d, $J = 8.5$ Hz, H-2′ and H-6′), 6.91 (d, $J = 8.5$ Hz, H-3′ and H-5′), 11.73 (s, 5-OH). Data unreported ^{13}C NMR (100 MHz, Me_2CO-d_6): 83.4 (C-2), 72.2 (C-3), 197.4 (C-4), 164.1 (C-5), 96.0 (C-6), 166.8 (C-7), 95.1 (C-8), 163.3 (C-9), 100.6 (C-10), 128.3 (C-1′), 129.3 (C-2′), 114.9 (C-3′), 157.9 (C-4′), 114.9 (C-5′), 129.3 (C-6′).

4. Chemotaxonomic significance

This is the first report on the compounds **1a**/**1b**, **2a**/**2b**, and **3** from a natural source. Compound **4** could be an artefact from **6**. HPLC analysis (mobile solvent: MeOH–H_2O 1:1; PDA detection: 230 nm; flow rate: 2 mL/min; column: Nucleosil C-18, 5 μm, 250 mm × 4.0 mm) revealed the absence of **4** in the crude CH_2Cl_2 extract. Dihydrokaempferol **5** is found in *Pterocaulon* species for the first time. Compound **6** has been isolated previously from *P. alopecuroides* (Vilegas et al., 1995), *Pterocaulon balansae* (Magalhaes et al., 1981), *Pterocaulon lanatum* (Magalhaes et al., 1981), and *Pterocaulon virgatum* (Debenedetti et al., 1998).

Various flavonoids have been previously described for *Pterocaulon* species, comprising flavonols (Debenedetti et al., 1987, 1994; Semple et al., 1999; Kanlayavattanakul et al., 2003; Heemann et al., 2006), flavanones (Alarcón et al., 2008; Macleod and Rasmussen, 1999) and dihydroflavonols (Alarcón et al., 2008; Bohlmann et al., 1981; Heemann et al., 2006; Vilegas et al., 1995). The results obtained in this work show that *P. alopecuroides* is a plant with a high polyphenol secondary metabolism and with a terpenoid side chain incorporation at C-7 into the flavonoid skeleton. Until this study, only two flavonoids with 7-O-prenylation at ring A have been reported in the genera *Pterocaulon*: 7-O-prenyltaxifolin from *P. virgatum* (Bohlmann et al., 1981), *P. alopecuroides* (Alarcón et al., 2008; Vilegas et al., 1995) and *Pterocaulon interruptum* (Heemann et al., 2006), and 7-O-prenylaromadendrin from *P. virgatum* (Bohlmann et al., 1981) and *P. alopecuroides* (Alarcón et al., 2008). More investigations on flavonoids of species of *Pterocaulon* will be carried out in order to further establish the chemotaxonomic significance of 7-O-prenyl flavonoids in *Pterocaulon* genus.

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