



## Flavanone glycosides from *Bidens gardneri* Bak. (Asteraceae)



Denise Brentan Silva<sup>a,b</sup>, Laura Tiemi Okano<sup>c</sup>, Norberto P. Lopes<sup>b,\*</sup>, Dionéia C.R. de Oliveira<sup>b,\*</sup>

<sup>a</sup> *Lychnoflora Pesquisa e Desenvolvimento em Produtos Naturais LTDA, Campus USP, Ribeirão Preto, SP, Brazil*

<sup>b</sup> *Núcleo de Pesquisa em Produtos Naturais e Sintéticos (NPPNS), Faculdade de Ciências Farmacêuticas de Ribeirão Preto – Universidade de São Paulo, Ribeirão Preto, SP, Brazil*

<sup>c</sup> *Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Ribeirão Preto, Universidade de São Paulo, SP, Brazil*

### ARTICLE INFO

#### Article history:

Received 22 January 2012

Received in revised form 28 June 2013

Available online 24 October 2013

#### Keywords:

*Bidens gardneri*

Asteraceae

Flavanones

LC–MS

### ABSTRACT

LC–DAD–MS/MS analysis of the Brazilian medicinal plant *Bidens gardneri* Bak. (Asteraceae) results in identification of eleven phenolic compounds. HRESIMS, MS/MS and UV data analyses, with phytochemicals isolation guided by MS data, results in flavanones–(–)-4'-methoxy-7-O-β-D-glucopyranosyl-8,3'-dihydroxyflavanone; (–)-7-O-(6''-E-p-coumaroyl)-β-D-glucopyranosyl-8,3',4'-trihydroxyflavanone; and (–)-4'-methoxy-7-O-(6''-acetyl)-β-D-glucopyranosyl-8,3'-dihydroxyflavanone being identified-together with four known compounds. The absolute configurations of two of the flavanones were determined as 2S via circular dichroism.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

*Bidens gardneri* Bark (tribe Heliantheae, subtribe Coreopsidinae, family Asteraceae), popular known as “picão”, is used as a diuretic. It is also employed to treat ulcer, fever, and icterus (Pott and Pott, 1994). Most of the chemical constituents of *B. gardneri* are unknown and Silva et al. (2010) only reported the composition of its essential oil. Different flavonoids were isolated from *Bidens*, some of which showed biological activities including antiviral (Tommasi et al., 1997), stimulation of IFN-γ expression (Chang et al., 2007), and antioxidant (Venkateswarlu et al., 2004) properties amongst and others. In addition, chalcones, flavanols and aurones are the main flavonoids isolated from *Bidens* species (see Supplementary data). In this study, a rapid identification by LC–DAD–MS was used to analyze a collection of Asteraceae plant extracts and to guide the isolation of new compounds. Reported herein is the isolation of seven compounds, and identification of eleven compounds from *B. gardneri* by LC–DAD–MS/MS.

## 2. Results and discussion

The EtOAc extract of *B. gardneri* was analyzed by LC–DAD–MS and LC–DAD–MS/MS. On the basis of MS, MS/MS, and UV spectroscopic analyses and comparison with fragmentation patterns previously published for chlorogenic acid derivatives and

flavonoids it was possible to identify 11 phenolic compounds (Fig. 1, Table 1S) including vanods new metabolites including possible new metabolites. To isolate the new metabolites, the EtOAc extract was subjected to Sephadex LH-20<sup>®</sup> column chromatography; the fractions of interest yielded three new flavanones **8**, **9** and **11** in addition to eight other (known) compounds. (Fig. 2).

The UV spectra of compounds **8**, **9**, and **11** had two bands with maximum absorptions near 285 and 335 nm (shoulder), typical of flavanones or dihydroflavonols (Markham, 1982). However, in a survey of flavonoids in *Bidens* there is no reported dihydroflavonols, indicating that these compounds are probably flavanones (Fig. 1S). The molecular formulae were obtained with the accurate mass of each compound determined (Table 1S). The product ion spectra of the flavanones also provided information about the specific A- and B-ring fragmentation pathway, such as the retro-Diels–Alder fragmentation reaction, which are diagnostic ions for the A- and B-ring substitution pattern (Fabre et al., 2001; March et al., 2006). A literature survey using molecular formula, type of flavonoid (flavanone), and the possible fragmentation pattern however, gave no hints. Therefore, the fractions containing the compounds of interest was investigated by LC–DAD analysis and this technique was used to monitor the isolation of these compounds.

The <sup>1</sup>H NMR spectra of **8**, **9**, and **11** were similar to those of flavanones, where the chemical shift of C-3' and C-4' confirms the presence of a 3',4'-disubstituted B-ring; also verified was the occurrence of two *ortho*-hydrogen in the A-ring (*J* ≈ 9 Hz), there being correlated with each other in COSY spectra (Table 2). The lack of a signal at 12 ppm (chelated 5-hydroxy proton), the downfield shift of C-10 (+ 14 ppm), and the shielding of C-4 (carbonyl)

\* Corresponding authors. Address: Universidade de São Paulo, Faculdade de Ciências Farmacêuticas de Ribeirão Preto, Departamento de Física e Química, Brazil. Tel.: +55 16 3602 4252; fax: +55 16 3602 4243.

E-mail addresses: [npelopes@fcrp.usp.br](mailto:npelopes@fcrp.usp.br) (N.P. Lopes), [drolivei@fcrp.usp.br](mailto:drolivei@fcrp.usp.br) (D.C.R. de Oliveira).

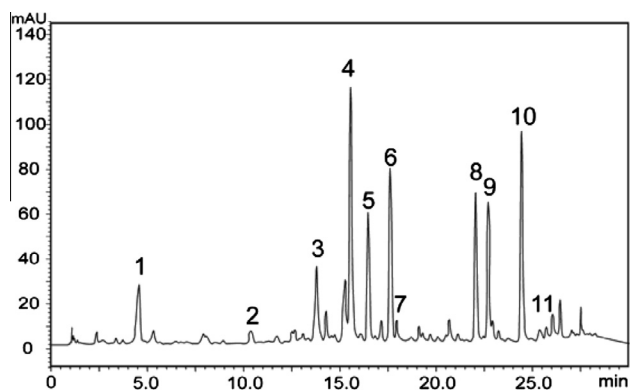


Fig. 1. LC-DAD profile of the extract from *Bidens gardneri* and the identified compounds (1–11, see Fig. 2 for structures).

attested to the absence of a 5-OH group. (Vasconcelos et al., 1998; Agrawal et al., 1989). The H-6, however, correlated with the carbon near  $\delta$  135 in the HMBC spectra, therefore this carbon was assigned to the C-8 position on the basis of the significant shielding effect, confirming the presence of a 7,8-disubstituted A-ring (Tommasi et al., 1997).

In addition, the shifts, multiplicities, and coupling constant of H-5 and H-6 agreed with the proposed A-ring substitution for this aglycone, which was reported in chemical investigations of *Bidens* (Wang et al., 1997; Serbin et al., 1975). The signals  $\delta$  5.4 ( $J \approx 3$  and

12 Hz, H-2), 3.1 ( $J \approx 12$  and 17 Hz, H-3<sub>ax</sub>), and 2.8 ( $J \approx 3$  and 17 Hz, H-3<sub>eq</sub>) were consistent with an AMX system typical of flavanones (the C-ring), and the coupling constants confirmed that H-2 is *axial* Table 1. Therefore, the isolated flavanones displayed the thermodynamically favorable conformation in which the C-2 phenyl group lies in any equatorial orientation. The doublet at  $\delta$  5.0 with  $J \approx 7.5$  Hz, the other resonances between  $\delta$  3 and 5, and the vicinal coupling constants suggested the presence of a  $\beta$ -glucopyranose moiety. The acylation site for compound **11** and the position of coumaric acid in compound **9** were inferred from the downfield shift of H-6'' (0.5–1 ppm) and C-6'' (2–3 ppm). The binding connectivities to the methyl, glucopyranosyl, coumaroyl, and acyl groups were confirmed through correlations observed in the HMBC spectra, such as those between anomeric protons (H-1'') and C-7 observed for all isolated flavanones (Table 2). The molecular formulae of flavanones **8**, **9**, and **11** were assigned as C<sub>22</sub>H<sub>24</sub>O<sub>11</sub> (observed:  $m/z$  463.1254 [M-H]<sup>-</sup>, calculated for C<sub>22</sub>H<sub>23</sub>O<sub>11</sub><sup>-</sup>, 463.1246), C<sub>30</sub>H<sub>28</sub>O<sub>13</sub> (observed:  $m/z$  595.1460 [M-H]<sup>-</sup>, calculated for C<sub>30</sub>H<sub>27</sub>O<sub>13</sub><sup>-</sup>, 595.1457), and C<sub>24</sub>H<sub>26</sub>O<sub>12</sub> (observed:  $m/z$  505.1343 [M-H]<sup>-</sup>, calculated for C<sub>24</sub>H<sub>25</sub>O<sub>12</sub><sup>-</sup>, 505.1351), respectively. The absolute configurations at C-2 were determined to be *S*, in case of compounds **9** and **11** by circular dichroism (CD) spectra see supplementary data) in comparison with known flavanones, such as (-)-naringenin (Giorgio et al., 2004) and (-)-butin (Chokchaisiri et al., 2009). A negative Cotton effect for  $\pi \rightarrow \pi^*$  ( $\lambda_{\max}$  290 nm) and a positive Cotton effect for  $n \rightarrow \pi^*$  ( $\lambda_{\max}$  330 nm) was observed, these being compatible with a 2*S* configuration, the most common one observed in natural flavanones (Slade et al., 2005). It was thus

Table 1  
<sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data of compounds **8**, **9**, and **11** (500 MHz).

Position	<b>8</b> <sup>a</sup>		<b>9</b> <sup>a</sup>		<b>11</b> <sup>b</sup>	
	$\delta_C$	$\delta_H$ (J in Hz)	$\delta_C$	$\delta_H$ (J in Hz)	$\delta_C$	$\delta_H$ (J in Hz)
2	80.2	5.47, dd (3.2, 11.7)	80.2	5.33, dd (2.7, 11.9)	79.9	5.45, dd (2.6, 12.3)
3 <sub>ax</sub>	43.8	3.10, dd (11.7, 16.8)	43.6	3.06, dd (11.9, 16.9)	44.3	3.13, dd (12.3, 16.8)
3 <sub>eq</sub>		2.83, dd (3.2, 16.8)		2.78, dd (2.7, 16.9)		2.71, dd (2.6, 16.8)
4	193.0	–	193.7	–	192.0	–
5	117.6	7.37, d (9.0)	117.9	7.30, d (9.1)	117.3	7.25, d (8.8)
6	109.8	6.92, d (9.0)	109.5	6.86, d (9.1)	109.5	6.82, d (8.8)
7	151.5	–	151.2	–	151.5	–
8	135.5	–	135.2	–	135.8	–
9	151.3	–	151.3	–	151.3	–
10	117.2	–	117.1	–	117.5	–
1'	132.0	–	130.7	–	132.5	–
2'	113.8	7.02, d (2.0)	114.2	6.97 (sl)	115.1	6.97, d (1.3)
3'	146.7	–	145.2	–	147.4	–
4'	148.4	–	145.7	–	148.8	–
5'	111.5	6.93, d (8.2)	115.6	6.82, d (8.6)	112.8	6.94, d (8.3)
6'	118.3	6.96, dd (2.0, 8.2)	118.8	6.83, br d (8.6)	118.6	6.91, dd (1.3, 8.3)
1''	101.8	4.95 <sup>c</sup>	100.9	5.05, d (7.8)	101.8	4.89, d (7.2)
2''	73.7	3.53, t (8.8)	73.5	3.63, t (7.8)	73.9	3.34, t (8.4) <sup>d</sup>
3''	76.4	3.49, t (8.8)	76.2	3.59, t (9.0)	74.7	3.64, t (8.4) <sup>d</sup>
4''	70.2	3.41, t (8.8)	70.9	3.48, t (9.0)	70.7	3.20, t (8.4) <sup>d</sup>
5''	77.4	3.46 (m)	74.5	3.83 (m)	76.3	3.32 <sup>c</sup>
6''	61.3	3.89, br d (12.1)	63.8	4.37, dd (7.1, 11.5)	64.1	4.25, br d (11.5) <sup>d</sup>
		3.71, dd (5.2, 12.1)		4.55, db (11.5)		4.09, dd (6.5, 11.5) <sup>d</sup>
1'''	–	–	126.2	–	–	–
2'''	–	–	130.5	7.44, d (8.4)	–	–
3'''	–	–	116.1	6.85, d (8.4)	–	–
4'''	–	–	159.9	–	–	–
5'''	–	–	146.2	7.58, d (15.8)	–	–
6'''	–	–	113.8	6.30, d (15.8)	–	–
7'''	–	–	168.4	–	–	–
OCH <sub>3</sub> -4'	55.4	3.86, s	–	–	56.5	3.78, s
CH <sub>3</sub> (Ac)	–	–	–	–	21.5	2.02, s
C=O (Ac)	–	–	–	–	171.3	–

<sup>a</sup> Measured in CD<sub>3</sub>OD.

<sup>b</sup> Measured in DMSO-d<sub>6</sub>.

<sup>c</sup> Overlap signals and obtained from HMQC.

<sup>d</sup> Signals observed in the spectrum after D<sub>2</sub>O addition.

Download English Version:

<https://daneshyari.com/en/article/5164848>

Download Persian Version:

<https://daneshyari.com/article/5164848>

[Daneshyari.com](https://daneshyari.com)