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Isoflavones and flavonols from *Andira humilis*

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1. Subject and source

The genus *Andira* (Fabaceae), consisting of about thirty species, is distributed in tropical areas of the American and African continents (Matos, 1979; Pennington and Lima, 1995). Twenty-seven species of this genus are known to occur in Brazil, mostly in the Amazonian region, where they are popularly known as "angelim". *Andira humilis* Mart. ex Benth., commonly known as "angelim-rasteiro" and "angelim-do-campo", is a shrub found in the Brazilian "Cerrado" (Almeida et al., 1998). The root of this plant was collected in November 2003 in Campo Grande, Mato Grosso do Sul, Brazil. The plant material was identified by MSc. Ubirazilda M. Resende of the CGMS Herbarium of the Universidade Federal de Mato Grosso do Sul, Brazil, where a voucher specimen (no. 11505) was deposited.

2. Previous work

No phytochemical or biological studies have been previously reported for *Andira humilis*. However, previous works on this genus revealed the occurrence of isoflavonoids from *A. inermis* (Cocker et al., 1962; Lock de Ugaz et al., 1991; Kraft et al., 2000, 2002; Silva et al., 2000), *A. anthelmia* (Silva et al., 2007, 2008), *A. fraxinifolia* (Silva et al., 2006), *A. surinamensis* (Almeida et al., 2008) and *A. parviflora* (Braz-Filho et al., 1973), being isoflavones and their glycosides the most representative components. Some of these compounds have shown antiplasmodial and anthelmintic properties (Kraft et al., 2000; Silva et al., 2008). A few triterpenoids (Silva et al., 2006, 2007; Almeida et al., 2008), flavonol and flavanonol glycosides (Lock de Ugaz et al., 1991; Silva et al., 2000, 2006, 2007; Kraft et al., 2001), in addition to 2-aryl-3-hydroxymethyl-benzofuran (Kraft et al., 2002) and three

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Table 1
In vitro antifungal activity of compounds **1**–**5**.

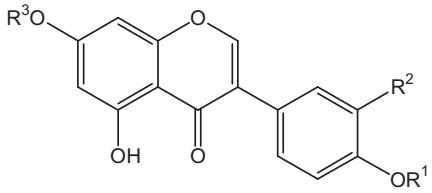
Compound	MIC (μg/mL)				
	Candida krusei ATCC 6258	*C. glabrata* ATCC 9030	*C. albicans* ATCC 90028	*C. parapsilosis* ATCC 22019	*Cryptococcus neoformans* ATCC 32045
1	I	I	I	I	I
2	200	200	200	200	200
3	100	100	100	200	100
4	200	200	200	200	200
5	200	200	200	200	200
Amphotericin B	0.25	0.25	0.5	0.25	0.5

I: inactive (MIC > 200 μg/mL).

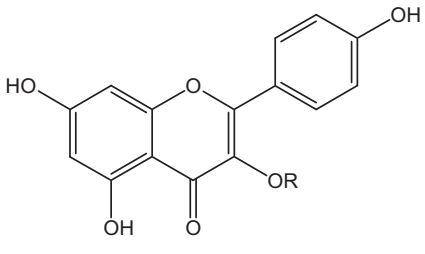
aryl-benzofuran-3-carbaldehyde derivatives (Kraft et al., 2001) have also been obtained and some of these derivatives have shown antiplasmodial activities (Kraft et al., 2001).

3. Present study

The air-dried and powdered roots (2000 g) were extracted at room temperature with EtOH. After concentration *in vacuo*, the residue was partitioned between hexane/CH_3CN/$CHCl_3$/H_2O (20:34:10:10). The hexane/$CHCl_3$ phase (10.0 g) was chromatographed over a silica gel column (63–200 μm) eluted successively with stepwise gradients of hexane/EtOAc and EtOAc/MeOH to yield eight fractions (I-VIII). Biochanin A (**1**, 39.0 mg) (Markham and Geiger, 1994; Agrawal and Bansal, 1989) was obtained from Fraction II (hexane/EtOAc 7:3, 150.6 mg). Fraction III (hexane/EtOAc 1:1, 1.9 g) was further separated by CC on Sephadex LH-20 ($CHCl_3$/MeOH 1:1) to give genistein (**6**, 17.2 mg), pratensein (**7**, 15.1 mg) and a mixture (20.0 mg) of **6**, **7** and dihydrogenistein (**10**) (Markham and Geiger, 1994; Agrawal and Bansal, 1989; Soidinsalo and Wähälä, 2004). The CH_3CN/H_2O phase (15.9 g) was subjected to CC on silica gel RP-18 (40–63 μm), using step gradient elution with H_2O/MeOH to afford ten fractions (A→J). Fraction A (H_2O, 2.1 g) was further separated by CC over silica gel (63–200 μm), eluted with $CHCl_3$/MeOH/H_2O



1 $R^1 = CH_3$, $R^2 = R^3 = H$
2 $R^1 = CH_3$, $R^2 = H$, R^3 = glu
3 $R^1 = CH_3$, $R^2 = H$, R^3 = xyl(1→6)glu
4 $R^1 = CH_3$, $R^2 = H$, R^3 = api(1→6)glu
5 $R^1 = CH_3$, $R^2 = H$, R^3 = api(1→5)api(1→6)glu
6 $R^1 = R^2 = R^3 = H$
7 $R^1 = CH_3$, $R^2 = OH$, $R^3 = H$



8 R = H
9 R = rha(1→6)[xyl(1→2)]gal

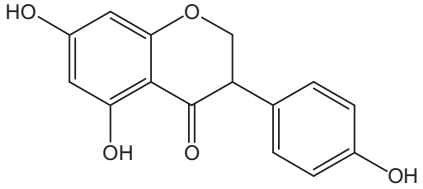


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Fig. 1. Chemical structures of the flavonoids and isoflavonoids isolated from the roots of *A. humilis*.