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Constituents of *Moquinia kingii*

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Extraction of the constituents of total plant (aerial parts and roots) of Moquinia kingii *afforded three flavonoids described for the first time in the tribe Moquinieae. In addition sesquiterpene lactone and triterpenes were isolated. Structures were established by spectroscopic studies.*

Uniterms
- *Moquinia kingii*
- Asteraceae
- Sesquiterpene lactone
- Flavonoids

INTRODUCTION

The tribe Moquinieae is endemic to Brazil and its species are distributed in Minas Gerais, Espírito Santo and Bahia states and comprises two genera, *Pseudostifftia* and *Moquinia* (Robinson, 1999). Both are monotypic genera and *Moquinia* is represented by *Moquinia racemosa*, whereas *Pseudostifftia* by *Pseudostiffitia kingii*, synonymy *Moquinia kingii*.

In 1990, Gamerro described *Pseudostifftia* H. Robinson as synonymy of *Moquinia.* Thus this genus comprises now two species and in addition, there is a new combination *Moquinia kingii* (H. Robinson) Gamerro.

Bremer (1994) described two species for *Moquinia*, in accordance to Gamerro (1990) in the tribe Vernonieae. In the same year, Robinson presented a new tribe Moquinieae based in studies of the spinose pollen and the comparatively short and unsclerified apical anther appendage. Thus, the description in the Vernonieae of *Pseudostifftia* from Brazil was followed by the addition of the related Moquinia DC and then by the transfer of both genera to the new tribe Moquinieae (Robinson, 1999).

Acetylenes and triterpenes (Bohlmann *et al.*, 1980), guaianolides (Bohlmann *et al.,* 1982), and diol acyclic sesquiterpene (Bohlmann, Jakupovic, 1990) have been detected in the species *Pseudostifftia kingii*.

Tripanocidal and antimicrobial activities of the crude extract, cynaropicrin and apigenin from *M. kingii,* were previously reported by Schinor *et al.* (2004), showing significant activity against the trypomastigote forms of *Trypanosoma cruzi*, as well as against the gram-positive bacteria and yeast strains.

In this work, the main compound isolated from *M. kingii* was cynaropicrin, the same sesquiterpene lactone (guaianolide) obtained from *P. kingii*, by Bohlmann *et al.* (1982). In addition, apigenin, luteolin, quercetin, lupeol and lupeol acetate were also isolated of the crude extracts. Flavonoids have been described for the first time in this tribe.

MATERIAL AND METHODS

Plant material

The species *Moquinia kingii* was collected by Walter Vichnewski in Pico das Almas (Bahia) in April 1996 and identified by Prof. Dr. João Semir (Departamento de Botânica, Universidade de Campinas, SP) and a voucher specimen (UEC 35137) was deposited at the Herbarium of this University.

General experimental procedures

^{1}H and ^{13}C NMR spectra were recorded in Bruker Avance-DRX spectrometer operating a frequency of

400 MHz and 100 MHz, respectively. TLC were carried out on silica gel plates (Merck) GF_{254} and Hex/EtOAc 8:2, Hex/EtOAc 3:7, EtOAc/MeOH 7:3 for triterpenes, sesquiterpene lactone and flavonoids, respectively. All compounds were visualized using H_2SO_4 followed by heating. Column Chromatography was performed on a normal silica gel 60 (Merck) using hexane, ethyl acetate, methanol and mixture of these solvents as eluents. Gas chromatographic analysis was performed in a Hewlett-Packard model 5890 Series II Gas Chromatograph with a split injector (split ratio 1:60) at 260 °C. The detector temperature was 330 °C. The injected volume was 2 mL. Hydrogen was employed as carrier gas at an average linear velocity of 44 cm/s (HP-50) and 42 cm/s (HP-1). The HP-50 (cross-linked 50% phenyl-methyl-silicone, 30 m x 0.25 mm x 0.25 mm) and HP-1 (cross-linked methyl-silicone, 30 m x 0.25 mm x 0.25 mm) capillary columns were employed. For HP-50 the column temperature was 280 °C (isotherm) and for HP-1 the column temperature program was 250 °C held for 12 min, increased at 6 °C/min to 280 °C, and held this temperature for 30 min. Data were processed on a Hewlett-Packard model 3395 injector. Standard triterpenes: authentic tritepenes isolated from different plant material in our laboratory were used as standard. Cholesterol was used as internal standard.

Extraction and isolation

Dried and pulverized aerial parts of *M.kingii* (2.1kg) were exhaustively extracted with chloroform and ethanol, successively, at room temperature. The solvents used in each extraction were evaporated under reduced pressure and the crude chloroform extract (80.42 g) was suspended in MeOH-H_2O 9:1 and partitioned with hexane and chloroform.

The chloroformic fraction (18.50 g) was chromatographed on silica gel 60 column chromatography and twenty-three fractions were collected. All fractions were monitored by TLC and purified by preparative TLC and recrystallization. The chloroformic fraction yielded: 60 mg of apigenin **(1)**, 22 mg of lupeol **(2),** 15 mg of lupeol acetate **(3)** and 70 mg of cynaropicrin **(4)**.

The crude EtOH extract (40.65 g) was partitioned with dichloromethane and methanol and after evaporation of the solvent under reduced pressure, the dichloromethane fraction (8.01g) was fractionated on silica gel 60 column chromatography, yielding 38 mg of apigenin **(1)**, 90 mg of luteolin **(5)** and 30 mg of quercetin **(6)**.

RESULTS AND DISCUSSION

Compounds **1**, **5** and **6** were identified by comparison of spectral data with the reported values (Mabry *et al*., 1970). Compounds **2** and **3** were identified by HRGC and co-injection with authentic standard. The guaianolide **4** (Figure 1) was identified by comparison ^1H NMR spectral data with reported values in literature (Bohlmann *et al.*, 1982). HMQC and ^1H-^1H COSY spectral data (Tables I and II) were determined and reported for the first time.

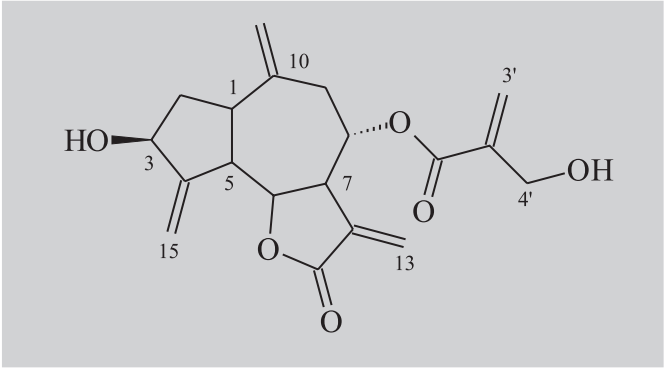

FIGURE 1 - Chemical structure of the compound **4**.

The triterpenes **2** and **3**, of natural occurrence in many plants, mainly in Asteraceae, have shown several biological activities. Lupeol has been demonstrated antitumoral, antioxidant, cytotoxic and diuretic (Noldin *el al.*, 2003) activities. Compounds **1**, **5** and **6**, are characterized mainly as antioxidants and this activity for quercetin has been comparable to the potent food antioxidant TBHQ (Arora *et al.*, 1998).

Cynaropicrin **4** is found in many species of Asteraceae. The sesquiterpene lactones are usually characterized by a α-methylene-γ-lactone group, which may react with sulphydryl group of proteins by a Michael addition (Milbrodt *et al.*, 1997). The reaction between these groups could be responsible for the toxic of effect sesquiterpene lactones (Noldin *et al.*, 2003). This compound showed 89% lysis against trypomastigote forms of *T. cruzi* in concentration of up to 100 mg/mL and inhibited the growth of gram-positive bacteria and yeast strains (Schinor *et al*., 2004).

Cynaropicrin was the main compound isolated from *M. kingii*, and it is the same sesquiterpene lactone, guaianolide, obtained from *Pseudostiffitia kingii*, by Bohlmann (1982). Thus both species, *M. kingii* and *P. kingii* can be synonymous, although *P. kingii* has presented other sesquiterpene lactones not found yet in *M. kingii*, maybe because the plants were collected in different habitat

TABLE I - ^{1}H-NMR spectral data for **4** (400 MHz, $CDCl_3$)

H	δ (ppm)	M	J (Hz)	Correlated with H
1	2.98	dd	11.5; 8.6	2α, 2β
2a	1.72	ddd	11.5; 12.5; 7.1	1, 2β, 3
2b	2.17	ddd	8.6; 12.5; 11.8	1, 2α, 3
3	4.53	dddd	11.8; 7.1; 1.7; 2.0	2α, 2β, 15α, 15β
5	2.85	ddl	10.6; 1.5	6, 15α, 15β
6	4.30	dd	10.6; 9.5	5, 7
7	3.24	dddd	9.5; 9.5; 3.0; 2.5	6, 8
8	5.13	ddd	9.5; 5.0; 3.5	7, 9α, 9β
9a	2.71	dd	5.0; 14.8	8, 9β
9b	2.40	dd	3.5; 14.8	8, 9α
13a	6.20	dd	3.0	7, 13β
13b	5.66	dd	2.5	7, 13α
14a	5.46	d	1.2	14α
14b	5.36	d	1.2	14β
15a	5.15	ddd	1.7; 1.5;	3, 5, 15β
15b	4.93	ddd	2.0; 1.5	3, 5, 15α
3'a	6.35	dd	3.0; 1.2	4', 3'β
3'b	6.00	dd	3.0; 1.5	4', 3'α
4'	4.35	d	1.2	3'α

TABLE II - ^{13}C-NMR spectral data for **4** (75 MHz, $CDCl_3$)[a]

H	**δ (ppm)**	**HMQC**
1	44.9 (*d*)	1
2	38.5 (*t*)	2α, 2β
3	72.8 (*d*)	3
4	151.7 (*s*)	—
5	50.9 (*d*)	5
6	78.6 (*d*)	6
7	47.2 (*d*)	7
8	74.0 (*d*)	8
9	36.4 (*t*)	9α, 9β
10	141.6 (*s*)	—
11	137.2 (*s*)	—
12	169.6 (*s*)	—
13	122.6 (*t*)	13α, 13β
14	117.8 (*t*)	14α, 14β
15	112.9 (*t*)	15α, 15β
1'	165.4 (*q*)	—
2'	139.5 (*q*)	—
3'	125.8 (*t*)	3'α, 3'β
4'	60.7 (*d*)	4'

[a] – multiplicities were determinate with assistance of DEPT 135° experiment.

and conditions of environment could interfere in the biosynthesis routes this compound (Spring, 1991).

The compounds **1**, **5** and **6**, are found in *M. kingii*, but there are no any reports for *P. kingii*. Therefore it is necessary more studies to support the synonymy of both genera.

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RESUMO

Constituintes de *Moquinia kingii*

A extração da planta total (partes aéreas e raiz) de Moquinia kingii *forneceu três flavonóides, descritos pela primeira vez na tribo Moquinieae, além de lactona sesquiterpênica e triterpenos. As estruturas foram determinadas por estudos espectroscópicos.*

Unitermos: *Moquinia kingii*. Asteraceae. Lactona sesquiterpênica. Flavonóides.

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