

## CONSTITUENTS OF *Mikania lasiandrae*

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*Mikania* Wild is the only genus in the subtribe Mikaniinae of the tribe Eupatorieae. It is represented by 415 species distributed mainly in Central and South America, with 171 species occurring in Brazil [1]. *M. glomerata* Spreng. (Compositae) is known popularly as "guaco" or "guaco-cheiroso" [2]. It is used in folk medicine for the treatment of the fever, rheumatism, and illnesses of the respiratory tract [3]. Pharmacological studies have confirmed the anti-inflammatory properties of the crude extract of the guaco, while chemical studies point to coumarins and *ent*-kaurenoic acid as the main constituents of this species [4, 5]. The occurrence of kaurane-type diterpenes and sesquiterpene lactones is very common in this genus [6, 7]. Diterpenes are predominant in the chemical composition of Brazilian *Mikania* [8]. The absence of chemical studies of *M. lasiandrae* DC., related to the necessity for a chemosystematic study of endemic species of the Brazilian flora, today considered a seriously threatened ecosystem, prompted us to isolate and identify the constituents of this species.

This paper reports the first study of the compounds of *Mikania lasiandrae* DC. (Asteraceae).

*Ent*-kaur-15(16)-en-19-oic acid (**1**), cinnamoylgrandifloric acid (**2**), lupeol (**3**),  $\beta$ -amyrin acetate (**4**),  $\alpha$ -amyrin acetate (**5**), friedelin (**6**), 12 $\beta$ ,16 $\beta$ -dihydroxy-19-*O*- $\beta$ -D-glucopyranosyl-*ent*-kaur-16-en-19-oic acid (**7**), caffeoylquinic acid (**8**), lupeol acetate (**9**), and friedelanol (**10**) were isolated as the main compounds of this plant.

The occurrence of diterpenes in the studied species is in accordance with the chemistry of species of *Mikania*. The glucoside diterpene is unknown in the genus, which can bring information that will contribute to the chemotaxonomic study.

The IR spectrum was recorded on a Nicolet Protege 460 spectrophotometer; NMR spectra were recorded on a Bruker DRX 400 spectrometer using TMS as internal standard. Column chromatography was performed over silica gel 70–230 (Merck). TLC analyses were performed on silica gel glass plates 60 GF<sub>254</sub> (Merck) and visualized under UV light and by spraying with sulfuric acid followed by heating (100–110°C).

The aerial parts from *Mikania lasiandrae* DC. were collected by Prof. Dr. N. P. Lopes in Campos de Jordao, SP, Brazil, in May 2000, and were identified by R. L. Esteves (Departamento de Biologia Animal e Vegetal, Universidade Estadual do Rio de Janeiro, RJ). Voucher specimens (NPL 268 and 271) are deposited at the Herbarium of the Departamento de Biologia, FFCLRP-Universidade de Sao Paulo, Brazil.

Dried and pulverized aerial parts of *M. lasiandrae* DC. (213g) were extracted at room temperature (ca. 25 °C) with CH<sub>2</sub>Cl<sub>2</sub> followed by MeOH to give 96 and 82 g of crude extract, respectively. The MeOH extract was partitioned first with MeOH–H<sub>2</sub>O (9 : 1) and then with C<sub>6</sub>H<sub>12</sub>, CH<sub>2</sub>Cl<sub>2</sub> and *n*-BuOH. The C<sub>6</sub>H<sub>12</sub>-soluble fraction (1.5 g) was chromatographed over Si gel 60 eluting with C<sub>6</sub>H<sub>12</sub> and gradually increasing the polarity with EtOAc and MeOH. Eighteen fractions were collected, monitored by TLC, and then re-chromatographed over Sephadex LH-20 using MeOH as eluent. This purification process furnished 2 mg of *ent*-kaur-15(16)-en-19-oic acid (**1**), 8 mg of cinnamoylgrandifloric acid (**2**), and a mixture (0.171g) of the following triterpenes: lupeol (**3**),  $\beta$ -amyrin acetate (**4**),  $\alpha$ -amyrin acetate (**5**), and friedelin (**6**).

The *n*-BuOH fraction (4.0 g) was chromatographed over Sephadex LH-20 eluting with MeOH. The collected fractions were monitored by TLC, furnishing 40 mg of the glucoside diterpene *ent*-19 $\beta$ -*O*-glycosyl, 12 $\beta$ ,16 $\beta$ -dihydroxykaurane (**7**), and 30 mg of caffeoylquinic acid (**8**).

From the crude CH<sub>2</sub>Cl<sub>2</sub> extract, 14 fractions were collected, giving the following compounds: 60 mg of **1** and 70 mg of a mixture of the triterpenes **3**, **4**, **5**, **6**, lupeol acetate (**9**), and friedelanol (**10**).

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Physical data, spectroscopic data ( $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR), and comparison with the data from the literature were utilized to identify the following compounds: **1** [9, 10], **2** [11], **7** [12, 13], and **8** [14].

The identities of all triterpenes were confirmed by GC analysis using authentic samples.

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