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Composition and bioactivity of *Pluchea carolinensis* (Jack.) G. essential oil from Martinique

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ABSTRACT

Pluchea carolinensis (Jacq.) G. Don (Asteraceae) is a plant species still widely used in the popular medicine of Caribbean region. The present work describes the chemical composition of essential oil of *P. carolinensis* leaves and flowers from Martinique Island and first exploration of its antimicrobial and insecticide activities. The chemical analysis using GC/FID and GC–MS of essential oils of *P. carolinensis* flowers and leaves led to the identification of 44 constituents representing 64.6–84.2 % of the extracts. The major identified components in aerial parts were selin-11-en-4α-ol (17.7–33.4 %), β-caryophyllene (5.5–21.1 %), 2,5-dimethoxycymene (8.9–3.3 %), caryophyllene oxide (6.6–3.3 %), α-pinene (4.7 %) and spathulenol (3.8–3.1 %). Furthermore, two carvotanacetone derivatives were for the first time identified from the aerial parts of *P. carolinensis*: 5-angeloyloxycarvotagetone (2.9–18.1 % of abundance in oils) and the new carvotanacetone 5-isovaleroyloxycarvotagetone (1.2–7.0 % of abundance in oils). Their structures were elucidated based on NMR and HRMS data. Essential oil of *P. carolinensis* exhibited an antimicrobial activity against *Aspergillus niger*, *Candida albicans, Staphylococcus aureus* and *Bacillus cereus*. Insecticidal assays against *Aedes aegypti* showed an interesting repellent activity at 1.0 % and a high irritating activity at 0.1 % against mosquitoes. Thus the essential oil from *P. carolinensis* aerial parts can be considered as new source of natural ingredient for pharmaceutical and cosmetical industries.

1. Introduction

Essential oils and their low molecular weight, highly volatile secondary metabolites (e.g. monoterpenoids, sesquiterpenoids) are well known for their medicinal properties, that is the reason why they are used in aromatherapy or prescribed to treat various health problems all over the world (Kerdudo et al., 2015; Raut and Karuppayil, 2014). *Pluchea carolinensis* (Jacq.) G. Don, commonly known as "cure for all", belongs to the Asteraceae family. This shrub grows naturally throughout the West Indies and from northern South America to Florida (Hodges and Bennett, 2006). The Martinique popular pharmacopoeia describes *P. carolinensis* (known as 'Djéri-tout', 'Guérit-tout' or 'Tabak diab') as a medicinal plant still widely used by rural population. Its most widespread usages are decoctions of aerial parts or leaves to fight against cold, rheumatism, fever, bronchitis, hepatic illness as well as to treat headache and other kind of pains (e.g. dental, stomach, thoracic) (Eldridge, 1975; Hussain et al., 2013; Longuefosse and Nossin, 1996). Some studies highlighted the biological activity of *P. carolinensis* extracts and confirmed its traditional uses. For instance, anti-microbial (Biabiany et al., 2013; Perera Córdova et al., 2006; Pérez et al., 2007), anti-oxidant (Fernández and Torres, 2006; Perera Córdova et al., 2014), and anti-leishmanial (García et al., 2011)

Abbreviations: GC, gaz chromatography; HPLC, high performance liquid chromatography; NMR, nuclear magnetic resonance; HRMS, high resolution mass spectroscopy.

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activities were demonstrated. These biological effects have been mainly attributed to characteristic compounds found in the *Pluchea* genus (Hussain et al., 2013). The most widespread metabolites in *P. carolinensis* are terpenoids. Monoterpenoids and eudesmane-type sesquiterpenoids (Ahmed et al., 1998; Pino et al., 2005, 2009) were reported in its aerial parts. Flavonoids including some that may be active against parasitic disease (García et al., 2011) and against pathogenic microorganisms (Perera Córdova et al., 2006) have been also characterized in *P carolinensis* leaves. Additionally, a number of caffeoylquinic acids derivatives were found in the aerial part of the plant (Hodges and Bennett, 2006; Hussain et al., 2013).

The composition of essential oil from leaves and flowers of *P. carolinensis* from Cuba island has been also investigated (Pino et al., 2005, 2009). The most prominent compound identified in the essential oil of leaves was juniper camphor (37.6 %), while in flowers it was selin-11-en-4α-ol (43.4 %). Other differences between both oils were the presence of additional major components in the flower oil such as 2,5-dimethoxy-*p*-cymene (12.5 %), neryl isovalerate (6.4 %) and caryophyllene oxide (6.8 %). It is worthwhile to note that other major compounds from flowers and leave essential oils remains unidentified in Pino et al. (2005, 2009) works. In the current study we report isolation, structure elucidation, antibacterial and insecticide activities of two new carvotanacetone derivatives from this essential oil. We also compare the chemical composition of the volatile compounds from the leaves and flowers of *P. carolinensis* using combination of analytical tools GC/FID, GC–MS and evaluate for the first time their biological activities. Antimicrobial activity was evaluated against several strains and insecticidal effect against *Aedes aegypti*.

2. Materials and methods

2.1. Plant material

The aerial parts (flowers and leaves) of *P. carolinensis* were collected in March 2012 (flowered stems) and October 2013 (leaves and stems) in Emeraude Domain (Morne-Rouge, Martinique, French Caribbean). Before extraction, plant material was dried at 45 °C until obtaining a rate of humidity lower than 10 %. Plant material was botanically authenticated by specialist of the Regional Natural Park of Martinique (Alex Clodius) and specimens (7-28032012) have been deposited at the Regional Botanical Conservatory of Martinique.

2.2. Plant extraction

The *P. carolinensis* essential oil of flowers or leaves was extracted by hydrodistillation (200–500 g of dried sample in a 3L reactor) for 6 h using a Clevenger apparatus. Ether petroleum was used in order to recover the sticky oil from the Clevenger. The solution was then dried with anhydrous $MgSO_4$ and the ether petroleum was evaporated (0.11 % yield). The obtained yellow essential oil was stored at 4 °C.

2.3. Olfactory analysis

Static evaluation was carried out by trained evaluators: perfumers and flavor chemist (Payan Bertrand S.A., Grasse, France). Samples were prepared at 10 % in EtOH 96%.

2.4. GC/FID analysis

The GC/FID analyses were performed using an Agilent 6890 N gas chromatograph equipped with a flame-ionization detector (FID), an electronic pressure control (EPC) SSL injector (Agilent Technologies, J&W Scientific Products, Palo Alto, CA, USA), and an apolar HP-1 capillary column (100% polymethylsiloxane; 0.2 mm × 50 m; film thickness, 0.33 μm). The oven temperature was programmed rising from 40 to 220 °C at 2 °C/min, then increased to 270 °C at 20 °C/min and, finally, held isothermal at 270 °C for 20 min. Injector temperature was set at 220 °C and detector temperature at 280 °C. Split ratio was 1/100 and injection volume of 1 μL. Samples were injected in triplicate for quantitation.

2.5. GC–MS analysis

The GC–MS analyses were carried out with a gas chromatograph model Agilent 6890 (Palo Alto, CA) equipped with a mass selective detector MSD5975B (Agilent) and a multifunction automatic sampler (Combi-Pal, CTC Analytics, Zwingen, Swiss) using an HP-1 MS capillary column (100% polymethylsiloxane; 0.2 mm × 50 m; film thickness, 0.33 μm) and a CP-Wax 52CB column (100% polyethyleneglycol, 0.25 mm × 50m; film thickness, 0.20 μm). With the HP-1 MS column, the oven temperature was programmed rising from 40 to 220 °C at 2 °C/min, from 220 to 270 °C at 20 °C/min and kept isothermal at 270 °C for 20 min. With the CP-Wax 52CB column, the oven temperature was programmed rising from 40 to 240 °C at 2 °C/min, and kept isothermal at 240 °C for 10 min. Carrier gas was Helium (constant flow: 1 mL/min); ionization voltage, 70 eV; scan time, 1 s; mass range, 40–300 amu. Split ratio was 1/100, injector temperature 250 °C with an injection volume of 1 μL.

2.6. Compound identification based on gas chromatography data

The identification of the volatile compounds was based on the comparison of (i) their recorded mass spectra with those listed in the mass-spectral libraries Wiley 07 (7th edn.) and IST/EPA/NIH (NIST 05), libraries from the laboratory and those published (Adams, 2004; Boelens, 1999; Joulain et al., 2001; McLafferty and Stauffer, 1989) and (ii) their retention indices (RIs), determined relative to the retention times (tR) of a series of *n*-alkanes (C_8–C_{30}), with those of the literature.

The contents of all constituents expressed in percentages were determined from their GC-FID peak areas without using correction factors.

2.7. Compound isolation

The essential oil was fractionated by Flash chromatography (Flash chromatography system, Grace) on silica gel (4 g) using petroleum ether (100%) and then petroleum ether–diethyl ether (50:50) to obtain two major fractions A and B, respectively. Fraction B was further fractionated on silica gel using gradient elution with petroleum ether–diethyl ether (from 95 to 5 to 60:40) leading to five fractions. Compounds **1** and **2** were eluted in fraction B-1 and B-2. Fraction B-3 gave compound **3**. Afterwards, unknown compounds (**1** and **2**) were isolated by semi-preparative HPLC using an Agilent 1200 system (Courtabeouf, France), equipped with DAD (Diode-Array detection) detector. Separation was performed in isocratic mode using a semi-preparative Luna C18 column (Phenomenex, 10 × 250 mm, 5 μm). Eluent was constituted of acetonitrile/water (60:40, v/v) both acidified at 0.1 % TFA. Flow rate was set at 4 mL/min and injection volume at 50 μL.

2.8. NMR analysis

NMR was carried out on Bruker Avance DRX500 (500 MHz) (Brucker, Wissembourg, France). The solvent was $CDCl_3$ (Eurisotop, Saint-Aubin, France); chemical shifts (δ) are given in parts per million (ppm), and coupling constants (*J*) are given in hertz.