Biochemical Systematics and Ecology 70 (2017) 7–13

Contents lists available at ScienceDirect

Biochemical Systematics and Ecology

journal homepage: www.elsevier.com/locate/biochemsyseco

Chemotaxonomic value of flavonoids in *Chromolaena congesta* (Asteraceae)

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ARTICLE INFO

Article history:
Received 16 May 2016
Received in revised form 20 October 2016
Accepted 22 October 2016

Keywords:
Asteraceae
Chromolaena congesta
Flavonoids
Chemotaxonomy

ABSTRACT

The phytochemical investigation on the aerial parts of *Chromolaena congesta* led to the isolation of nine flavonoids, known in the literature as genkwanin (**1**) kumatakenin (**2**) acacetin (**3**), kaempferol 3-methyl ether (**4**), apigenin (**5**), apigenin 5,7-dimethyl ether (**6**), apigenin 5-methyl ether (**7**), luteolin (**8**) and kaempferol (**9**). The chemical structures were established on the basis of spectral evidence. All the compounds were isolated from this species for the first time. The results from the present study provide further information about the flavonoids as taxonomic marker of the genus *Chromolaena*, and the chemotaxonomic significance of these compounds were also summarized.

1. Subject and source

Chromolaena is one of the largest genera of the tribe Eupatorieae (Asteraceae), comprises 165 species (King and Robinson, 1987; Rodríguez-Cabeza et al., 2014), of which 70 occur in Brazil, and 45 are endemic (Oliveira, 2016). *Chromolaena congesta* (Hook. & Arn.) R.M.King & H. Rob is a shrub native of Brazil, distributed in the Northeast, Southeast and South regions. The plant material was collected at Ponta Grossa, Paraná, Brazil, in February 16th, 2012 and was identified by Dr. Marta Regina Barrotto do Carmo. A voucher specimen (HUPG. 18906) has been deposited in the herbarium of State University of Ponta Grossa, Brazil.

2. Previous work

Previous investigations on the chemical composition of other plants belonging to *Chromolaena* show that flavonoids are valuable chemical markers within this genus (Barua et al., 1978; Amaro-Luis and Delgado-Méndez, 1993; Torrenegra and Rodriguez, 2011).

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http://dx.doi.org/10.1016/j.bse.2016.10.013
0305-1978/

Furthermore, different classes of secondary metabolites were also found in species of *Chromolaena* such as sesquiterpene lactones, germacrenos, prostaglandins, alkaloids, fatty acids, triterpenes, labdanes and steroids (Bohlmann et al., 1981a; de Gutiérrez et al., 1995; Gómez-Hurtado et al., 2011). However, there are no reports on the chemistry of *C. congesta*.

3. Present study

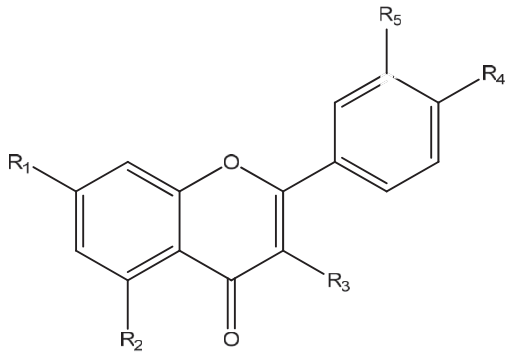
The air-dried whole plants of *C. congesta* (200 g) was extracted exhaustively with ethanol. After organic solvent removal, the crude extract obtained mass was 10.50 g. The resulting extract was suspended in MeOH:H_2O (1:1) and successively fractionated with n-hexane, $CHCl_3$, EtOAc and n-BuOH, respectively. The chloroformic soluble portion (2.53 g) was subjected to chromatography column (CC) on silica gel, using n-hexane, $CHCl_3$, EtOAc and MeOH in order of increasing polarity as eluent to give eight fractions (F1 − F8).

The fraction F3 (0.199 g) was processed by a silica gel CC with mobile phase of hexane and acetone in gradient elution to give eighteen sub-fractions (F3-1 to F3-18). Sub-fraction F3-12 to yield compounds **1**, **2** and **3** (7.1 mg) characterized in admixture. However, compound **2** was subsequently isolated. The sub-fraction F3-10 (31.5 mg) was purified by Sephadex LH-20 eluted with MeOH to yield five sub-fractions (F3-10-1 to F3-10-5). Sub-fraction F3-10-5 to yield compound **4** (6.4 mg).

The fraction F6 (1.026 g) was processed by a silica gel CC with mobile phase of hexane, AcOEt and MeOH in gradient elution to give fourteen sub-fractions (F6-1 until F6-14). Sub-fraction F6-1 to yield compound **5** (5.3 mg) and the sub-fraction F6-9 was purified by recrystallization in MeOH to yield compound **6** (5.5 mg). The sub-fraction F6-10 was purified by Sephadex LH-20, eluted with MeOH to yield seven new fractions. The sub-fraction F6-10-6 yield the compound **7** (5.3 mg).

Another part of the chloroformic fraction (52.5 mg) was subjected to column chromatography on Sephadex LH-20 and eluted with methanol to give sixteen fractions FS1 -FS16. Sub-fraction FS1-16 was found to be an **8** and **9** characterized in admixture (5.0 mg). The sub-fractions FS1-12 until FS1-15 (28.1 mg) were regrouped and purified by poly-vinylpolypyrrolidone (PVPP) column chromatography eluted with methanol to give seven new fractions. The sub-fraction FS1-1215-2 was identified the compound **2** (8.5 mg).

The structures were identified on the basis of their spectroscopic data (MS, 1D NMR and 2D NMR) and by comparison with those reported in the literature indicated that these compounds were genkwanin (**1**), (Gomes et al., 2011), kumatakenin (**2**) (Silva et al., 2009), acacetin (**3**) (Wawer and Zielinska, 2001), kaempferol 3-methyl ether (**4**) (Park et al., 2011), apigenin (**5**) (Zhou et al., 2014), apigenin 5,7-dimethyl ether (**6**) (Lin et al., 2007), apigenin 5-methyl ether (**7**) (Voigtländer and Balsam, 1970; Wagner et al., 1976), luteolin (**8**) (Markham et al., 1978) and kaempferol (**9**) (Markham et al., 1978). The structures of the flavonoids are presented on Fig. 1. The LC-MS analyses were carried out to different sub-fractions of chloroformic fraction, which showed the presence of apigenin as major compound.



Code	Compound	R_1	R_2	R_3	R_4	R_5
1	Genkwanin	OCH_3	OH	H	OH	H
2	Kumatakenin	OCH_3	OH	OCH_3	OH	H
3	Acacetin	OH	OH	H	OCH_3	H
4	Kaempferol 3-methyl ether	OH	OH	OCH_3	OH	H
5	Apigenin	OH	OH	H	OH	H
6	Apigenin 5,7-dimethyl ether	OCH_3	OCH_3	H	OH	H
7	Apigenin 5-methyl ether	OH	OCH_3	H	OH	H
8	Luteolin	OH	OH	H	OH	OH
9	Kaempferol	OH	OH	OH	OH	H

Fig. 1. Flavonoids from *Chromolaena congesta.*