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Chemical constituents of *Cardiospermum corindum* L. and their distribution in Sapindaceae

Fabiana L. Silva [a, *], Paulo R.H. Moreno [b], Raimundo Braz-Filho [c], Josean F. Tavares [a], José Maria Barbosa-Filho [a]

[a] Laboratory of Pharmaceutical Technology, University Federal of Paraiba, 58051-900 João Pessoa, PB, Brazil
[b] Institute of Chemistry, University of São Paulo, 05508-000 São Paulo, SP, Brazil
[c] Department of Natural Products Chemistry, University State of North Fluminense, 28013-600 Campos dos Goytacazes, RJ, Brazil

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ABSTRACT

Phytochemical investigation on the aerial parts of *Cardiospermum corindum* L. led to the isolation of two triterpenes [friedelin (**1**) and friedelinol (**2**)], two coumarins, [umbelliferone (**4**) and scopoletin (**5**)], three methoxylated flavones [umuhengerin (**3**), luteolin 3',4'-dimethyl ether (**6**) and chrysoeriol (**7**)], one non-cyanogenic glucoside [epidermin (**8**)] and one cyclitol [(*L*)-quebrachitol (**9**)]. To our knowledge, **2, 3, 6** and **8** were isolated for the first time within Sapindaceae. Of these classes of metabolites, the distribution of methoxylated flavonoids in *Cardiospermum* is reviewed, including the new records, indicating that polymethoxylated flavonoid (**3**) may be value as chemotaxonomic markers for this genus.

1. Subject and source

Cardiospermum L. is included into the Paullinieae tribe (Sapindoideae, Sapindaceae) and comprises 16 species of herbs, vines or suffrutescent herbs of pantropical distribution (Ferruci, 2000; Urdampilleta et al., 2012). Some species have important biological activities, such as anti-inflammatory, antipyretic, anti-arthritis (Sheeba and Asha, 2009), and are popularly employed in the treatment of central nervous system diseases (Kumar et al., 2011), rheumatism, and as a diuretic (Agra et al., 2008). *Cardiospermum corindum* L. was collected at the base of Pico do Jabre (7°15′34.27″ S, 37°23′8.53″ W), Paraiba, Brazil, in June 2009. The plant material was identified by Prof. Dr. Maria de Fátima Agra (UFPB). A voucher specimen (No. M.F. Agra et al. 6898) was deposited in the Herbarium Prof. Lauro Pires Xavier (JPB), at the same University.

2. Previous works

Previous phytochemical studies of *C. corindum* revealed the presence of 3′,4′-di-*O*-methyl luteolin-7-*β*-D-glucuronide (Adinarayana and Sarada, 1989; Rao et al., 1992), *myo*-inositol (Adinarayana and Sarada, 1989), 1-methyl 4-{[2-(4-nitrophenyl) ethenyl] sulfonyl}benzene, 1-{[2-methoxy-2 (4-nitrophenyl) ethyl] sulfonyl} 4-methyl-benzene (Adinarayana et al., 1987), *β*-sitosterol and stigmasterol (Adinarayana and Sarada, 1989).

* Corresponding author. Present address: Institute of Chemistry, University of São Paulo, 05508-000 São Paulo, SP, Brazil. Tel./fax: +55 11 3091 8226.
E-mail addresses: falimasilva@hotmail.com, fabianalima@ltf.ufpb.br (F.L. Silva).

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3. Present study

Air-dried and powdered *C. corindum* aerial parts (1102 g) were extracted exhaustively with 96% aqueous ethanol solution at room temperature. The combined extracts were filtered and concentrated under reduced pressure at 40 °C affording a crude extract (126.38 g). This extract was suspended in MeOH–H_2O (70:30 v/v) and successively fractionated with *n*-hexane, CH_2Cl_2 and *n*-BuOH. The CH_2Cl_2 extract (9.1 g) was subjected to CC on silica gel using step gradients of *n*-hexane-EtOAc and EtOAc-MeOH (system 1) to obtain 152 fractions combined according to their TLC profiles into 17 major fractions (Fr1-Fr17). Fraction Fr2 (0.12 g) was purified by prep. TLC (*n*-hexane-EtOAc, 95:5 v/v) to give (**1**) (90 mg). Fraction Fr3 (0.04 g) was subjected to silica gel CC using the system 1 to give a mixture of (**1**) and (**2**) (20 mg). From fraction Fr9, compound (**3**) (52 mg) was obtained as a precipitate after solvent drying. Fraction Fr10 (0.10 g) was subjected to silica gel CC using the system 1 and purified by prep. TLC (*n*-hexane-EtOAc, 60:40 v/v) to yield (**4**) (1 mg). While concentrating fraction Fr11 (0.05 g), a precipitate was formed which was then filtered under vacuum. The precipitate was refractionated by silica gel CC using the system 1 and purified by prep. TLC (*n*-hexane-EtOAc, 50:50 v/v) to give (**5**) (6.6 mg) and mixture of (**6**) and (**7**) (5.9 mg). Fraction Fr13 (0.09 g) was subjected to silica gel CC using system 1. Subfraction Fr13.1 was chromatographed in silica gel CC using gradient with $CHCl_3$–MeOH and purified by prep. TLC ($CHCl_3$–MeOH, 85:15 v/v) to yield (**8**) (12.8 mg). From fraction Fr15 obtained (**9**) (122 mg) as precipitate after solvent drying.

The structures of the isolated compounds (Fig. 1) were elucidated according to their spectroscopic data (IR, ^1H and ^{13}C NMR, one and two-dimensional techniques) and by comparison with those of literature. They were identified as friedelin (**1**) (Akihisa et al., 1992), friedelinol (**2**) (Salazar et al., 2000), umuhengerin (**3**) (Rwangabo et al., 1988), umbelliferone (**4**) (Liu and Tian, 2004), scopoletin (**5**) (Vasconcelos et al., 1998), luteolin 3′,4′-dimethyl ether (**6**) (Stevens et al., 1999), chrysoeriol (**7**) (Park et al., 2007), epidermin (**8**) (Lechtenberg et al., 1996) and (*L*)-quebrachitol,(**9**) (Huang and Luo, 1994).

4. Chemotaxonomic significance

Our phytochemical efforts on the CH_2Cl_2 extract of *Cardiospermum corindum* resulted in the isolation and identification of two triterpenes (**1, 2**), two coumarins (**4, 5**), three methoxylated flavones (**3, 6, 7**), one non-cyanogenic glucoside **(8**) and one cyclitol (**9**). This is the first report for compound **9** from *C. corindum*, compounds **1**–**6**, and **8** from a *Cardiospermum* species, and compounds **2**, **3, 6** and **8** in the Sapindaceae family (Fig. 1).

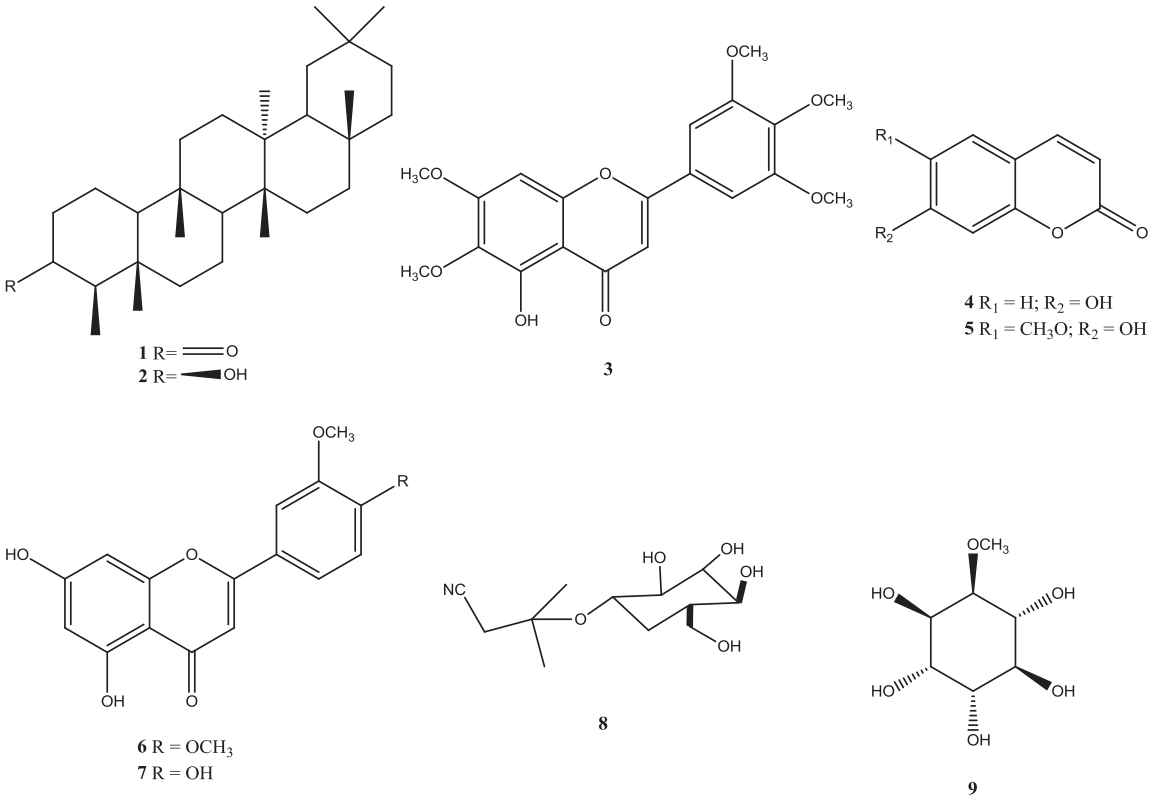

Fig. 1. Structures of compounds **1**–**9**.