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ScienceDirect
Biochemical Systematics and Ecology 36 (2008) 55–58
biochemical systematics and ecology
www.elsevier.com/locate/biochemsyseco

Occurrence of polygodial in species of *Polygonum* genus belonging to *Persicaria* section

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Received 1 February 2007; accepted 19 May 2007

Keywords: *Polygonum*; Polygodial; *Persicaria* section; Irritant glands

1. Subject and source

The genus *Polygonum* (Polygonaceae) is represented in Argentina by 20 species, which are divided into five sections: *Echinocaulon*, *Amblygonum*, *Persicaria*, *Tiniaria* and *Polygonum* (Cialdella, 1989; Gattuso, 2001). *Polygonum punctatum* Elliot, *Polygonum persicaria* L., *Polygonum acuminatum* Kunth., *Polygonum ferrugineum* Wedd., *Polygonum lapathifolium* L. and *Polygonum hydropiperoides* Michx. are six out of the 11 perennial herbs, of 30–100 cm height, belonging to the *Persicaria* section, which grow in the north-east and central lowlands of Argentina (Gattuso, 2000). *P. hydropiperoides* was collected during the flowering season (March 2005) in San Luis province, Merlo district (32°35′S Lat., 65°03′O Long. and 850 m elevation), identified by Elisa Petenatti, and deposited at the Herbarium, National University of San Luis (UNSL # 9256). The other five species were harvested in March 2005 in Santa Fe province, Puerto Gaboto district (32°27′S Lat., 60°48′O Long. and 25 m elevation), identified by Susana Gattuso and deposited at the Herbarium, National University of Rosario, Argentina (UNR Gattuso, S. 97, 108, 94, 99 and 115, respectively).

2. Previous work

The *Polygonum* genus is well known for producing a variety of secondary metabolites including flavonoids (Sartor et al., 1999; Peng et al., 2003; López et al., 2006), triterpenoids (Duwiejua et al., 1999), anthraquinones (Yim et al., 1998; Matsuda et al., 2001), coumarins (Sun and Sneden, 1999), phenylpropanoids (Murai et al., 2001; Takasaki et al., 2001), lignans (Kim et al., 1994), stilbenoids (Nonaka et al., 1982), and tannins (Wang et al., 2005). In addition, the pungent drimane-type sesquiterpene dialdehyde (−)-polygodial (Fig. 1) has been found in two species of the *Polygonum* genus: *P. punctatum* (de Almeida Alves et al., 2001) and *Polygonum*

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doi:10.1016/j.bse.2007.05.011

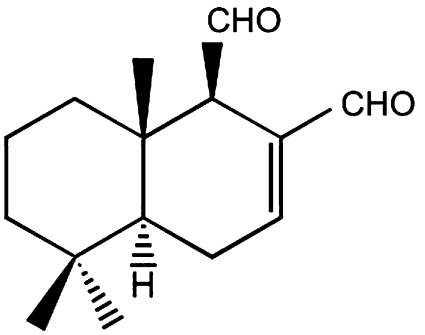

Fig. 1. Structure of polygodial.

hydropiper L. (Asakawa and Aratani, 1976). On the other hand, Hagendoorn et al. (1994) demonstrated that polygodial-containing organs of *P. hydropiper* produced and stored this irritant compound in specialized epidermic cavities named valvate or irritant glands. These secretory glands were afterwards suggested as an important distinguishing mark for the delimitation of the *Persicaria* section by Gattuso (2001) since they were found in seven out of the 11 species of this section growing in Argentina (Gattuso, 2001). At this point, it is interesting to note that both polygodial-containing species reported previously, *P. punctatum* and *P. hydropiper*, belong to the *Persicaria* section. Nevertheless, to the best of our knowledge there are no reports on the presence of polygodial neither in other species of this section nor in other species of the genus *Polygonum*. Polygodial plays an important role in

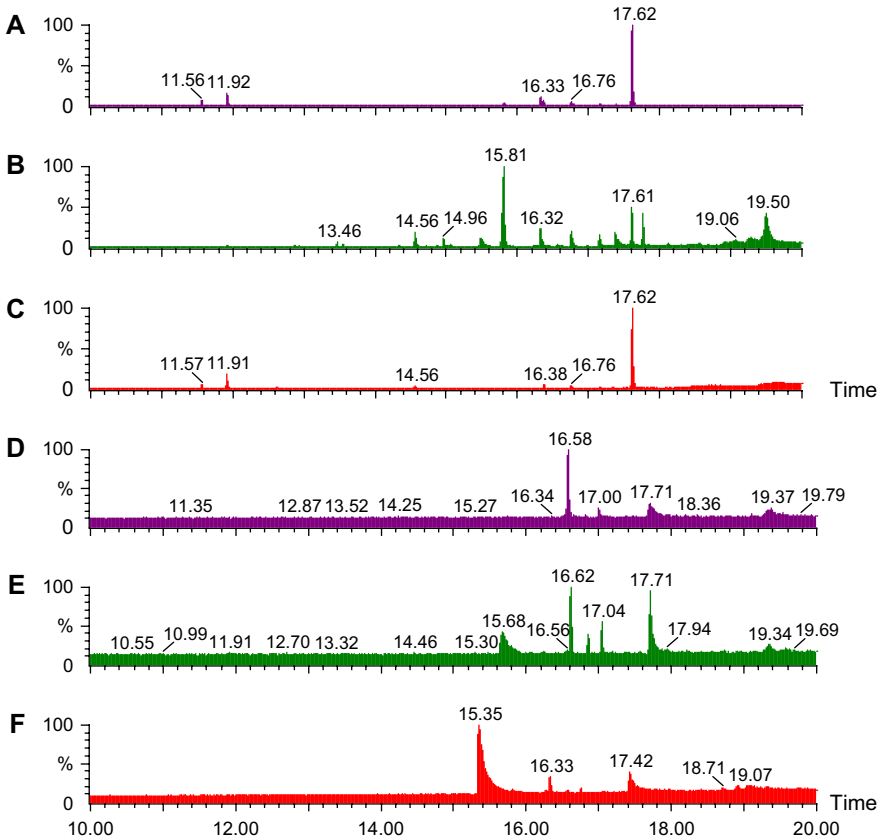

Fig. 2. GC spectra of dichloromethane extracts of *P. punctatum* (A), *P. persicaria* (B), *P. acuminatum* (C), *P. ferrugineum* (D), *P. lapathifolium* (E) and *P. hydropiperoides* (F). Peaks at 17.61/17.62 min in (A), (B) and (C) belong to polygodial.

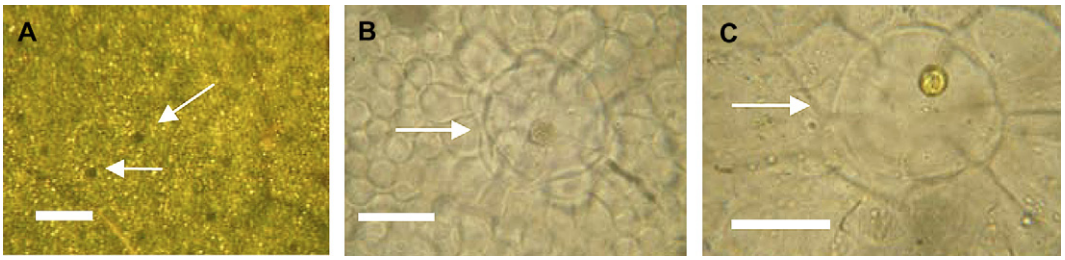

Fig. 3. Valvate glands (showed with white arrows) observed in the abaxial epidermis of leaves of *Polygonum persicaria* growing in Argentina. A: under magnifying glass; B and C: under light microscope. Bars: A: 100 μm; B and C: 20 μm. In C, the presence of the yellowish exudate is clearly observed.

plants' defense against predators (Cimino et al., 1985; Muratake et al., 1994), being fungitoxic (Kubo, 1988; de Almeida Alves et al., 2001), antifeedant against insects (Caprioli et al., 1987; Asakawa et al., 1988) as well as inhibitor of the transmission of some viruses (Asakawa et al., 1988).

3. Present study

Leaves of *P. punctatum*, *P. persicaria*, *P. acuminatum*, *P. ferrugineum*, *P. lapathifolium* and *P. hydropiperoides* (30 g each) were dried at room temperature (20 ± 2 °C), ground in a laboratory mill and macerated with dichloromethane for 24 h (3×). The solvent was evaporated under reduced pressure to yield 0.86, 1.14, 1.05, 0.80, 1.50 and 0.50 g of dichloromethane soluble-extracts, respectively. All extracts were submitted to GC–MS using a Turbo Mass Perkin Elmer chromatograph, equipped with a fused silica gel column (SE-30 25 m × 0.22 mm ID) with He as a carrier gas, coupled to a mass selective detector, film 0.25 μm, ionization energy 70 eV with a temperature programme of 70–200 °C at 10 °C/min; total time 30 min. Polygodial was identified by comparison of its retention time (17.62 min) and the MS spectrum with an authentic sample obtained from our previous works (Castelli et al., 2005; Malheiros et al., 2005). The linearity of the detector response was verified using a series of twofold diluted dichloromethane solutions of polygodial. The relationship between peak areas (detector responses) and concentration of polygodial was linear over 1000–31.2 μg/ml.

The analysis of the GC spectra clearly shows (Fig. 2 A–F) that *P. punctatum*, *P. persicaria* and *P. acuminatum* (but not *P. hydropiperoides*, *P. ferrugineum* and *P. lapathifolium*) contain polygodial in 0.11, 0.054 and 0.25 g/100 g on a dry weight basis, respectively. Leaves of each studied species were observed under both, a magnifying glass and an optical microscope (400 and 1000×, respectively) to corroborate the presence of the characteristic glands and correlate them with the occurrence of polygodial (Fig. 3). Interesting enough, valvate glands were observed only on the epidermis of the leaves of the three polygodial-containing species, which coincides with the previous report of Gattuso (2000). The finding of valvate glands in *P. persicaria* (Fig. 3) (which was concomitant with the presence of polygodial (Fig. 2B) was in accordance with the previous description of Gattuso (2000) and in contrast with the observation of Hagendoorn et al. (1994) who did not find neither polygodial nor glands in *P. persicaria*.

4. Chemotaxomic significance

The presence of polygodial in species of the section *Persicaria* of the genus *Polygonum* has an important taxonomic value for the infrageneric classification of the genus *Polygonum* into sections. So far, this natural sesquiterpene dialdehyde had been previously found only in two species of the *Persicaria* section (*P. punctatum*; de Almeida Alves et al., 2001, *P. hydropiper*; Hagendoorn et al., 1994), which in addition, contained the characteristic irritant glands in their leaves (Hagendoorn et al., 1994; Gattuso, 2000, 2001). As it is known, Hagendoorn et al. (1994) found a correlation between the presence of these cavities and of polygodial in *P. hydropiper*.

In the present study, we report for the first time the presence of polygodial in *P. acuminatum* and *P. persicaria* and found it again in *P. punctatum*. The three species (classified within the *Persicaria* section) showed to possess the characteristic glands described previously in most species of this section (Gattuso, 2001), adding new evidences on the correlation between polygodial and valvate glands. In addition, we determined the absence of polygodial in

P. ferrugineum, *P. lapathifolium*, and *P. hydropiperoides* which do not possess the characteristic valvate glands in their epidermic tissues.

Considering that Gattuso (2001) and Cialdella (1989) suggested a delimitation of the *Persicaria* section to those species of *Polygonum* genus containing the irritant valves, we suggest that the presence of polygodial (which can be easily detected by GC–MS) could be also of diagnostic value for the delimitation of the section *Persicaria*. Following this point of view, the inclusion of *P. hydropiperoides*, *P. ferrugineum* or *P. lapathifolium* (which do not possess neither polygodial nor valvate glands) within the *Persicaria* section could be the subject of a further revision.

Acknowledgements

S. Z. and S. G. are grateful to Agencia Nacional de Promoción Científica y Tecnológica (PICT R 260). M. D. acknowledges CONICET for a fellowship. This work is part of RIBIOFAR of CYTED.

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