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A set of biogenetically interesting polyhalogenated acetogenins from *Ptilonia magellanica*

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ABSTRACT

Ptilonines A–F, pyranosylmagellanicus D–E and magellenediol are previously undescribed acetogenins isolated from the red alga Ptilonia magellanica. Their structures were determined from spectroscopic evidence. The absolute configuration of the known pyranosylmagellanicus A, was established by derivatization with (R)– and (S)–α–methoxy –α–phenylacetic acids (MPA). Ptilonines exhibit an unusual halogenation pattern, that may confer evolutionary advantages to Ptilonia magellanica, for which a biogenetic origin is proposed. The antimicrobial effect of some of these compounds was evaluated.

1. Introduction

Within the Bonnemaisoniaceae family, seaweeds of the genus *Asparagopsis*, *Delisea*, *Bonnemaisonia* and *Ptilonia* have shown to be a rich source of polyhalogenated metabolites (Paul and Pohnert, 2011). The genus *Asparagopsis* releases a complex mixture of more than 120 halogenated compounds (McConnell and Fenical, 1980) possessing structures that contain up to 5 carbon atoms, including methane, acetones, propanols, butenones and acrylic and acetic acid derivatives. Genera such as *Delisea*, *Ptilonia*, and *Bonnemaisonia* display a variety of polyhalogenated compounds which contain seven and nine carbon atoms (Cueto et al., 1997), with the exception of one 12-carbon-atom metabolite (De Nys et al., 1992).

Six species of *Ptilonia* have been described to date. These species have a wide distribution ranging from the sub-Antarctic Islands to Australia, New Zealand, and Japan. All of them but one are from the Southern Hemisphere. Genera *Ptilonia* and *Delisea* were joined by Chihara and Yoshizaki, however, this merger was later refuted on the basis of differences in branch pattern, spermatangial sorus morphology, and cystocarp position (Chihara and Yoshizaki, 1978; Chihara, 1979; Bonin and Hawkes, 1988). With only two species studied: *P. australasica* and *P. magellanica* (Montagne) J. Agardh, 1852, the *Ptilonia* genus has been the least investigated among the Bonnemaisoneacea family.

P. australasica biosynthesized brominated γ-pyrone derivatives, 1,1,2-tribromoalk-1-enes with four and eight carbon atoms, some of which are related or identical to others isolated from *Delisea fimbriata* (Cueto et al., 1997; Rose et al., 1977), and polybrominated cyclopentenones of eight carbon atoms (Kazlauskas et al., 1978; Tran et al., 2016).

Studies on *P. magellanica* from Kergelen Islands produced the biosynthetically interesting 4-acetoxy-1,1-dibromo-2-heptanol **10** (Nicod et al., 1987), whereas *P. magellanica* collected from the Strait of Magellan yielded pyranosylmagellanicus A–C (**11**–**13**) and an

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acyclic halogenated nonaenone (Lorenzo et al., 2005), Fig. 1. Significant research has been carried out with natural furanones of *Delisea pulchra*, but excluding our preliminary study on *P. magellanica* (Lorenzo et al., 2005) and a more recent work on *P. australasica* (Tran et al., 2016), little additional work has been carried out in search of new related naturally occurring metabolites in the Bonmemaisoniacae family since 1997 (Ankisetty et al., 2004). Our interest in the chemistry of benthic organisms from the Chilean coast (Darias et al., 2001; Díaz et al., 2002; Díaz-Marrero et al., 2002, 2004) and in the scarcely studied *Ptilonia* genus, motivated us to re-examine a new extract of *P. magellanica* collected at the same place, since in the early work a mixture of metabolites was detected, requiring laborious separation.

In this study we have isolated and identified fifteen metabolites belonging to a single biosynthetic class. Compounds **1**–**9**, that include acyclic, **1**–**7**, and cyclic, **8**–**9** acetogenins, are described for the first time. In addition, compounds **10**–**14** (Lorenzo et al., 2005) were also re-isolated, along with the previously reported γ−pyrone **15** (Arnarp et al., 1990) Fig. 1.

The fifteen compounds depicted in Fig. 1 include all the metabolites isolated to date from *P. magellanica*. These were grouped into two classes according to the length of their main chain. One class possesses a long chain of seven carbon atoms, ptilonines A–F (**1**–**6**) and compound **10**, whereas the other class has nine carbon atoms, pyranosylmagellanicus A–E, magellenediol (**7**), **14** and **15**. The unnamed compounds **10** and **14** are now denominated ptiloninol and magellenone, respectively.

Reduced forms of heptenonas and nonanonas seem to be the major metabolites of *P. magellanica*. Surprisingly, all reported metabolites from *P. australasica* (Kazlauskas et al., 1978; Tran et al., 2016) possess a four or eight carbon atom main chain. This difference may constitute a taxonomical character useful to distinguish these two species.

2. Results and discussion

Compounds **1**–**15** were obtained from the crude extract of *Ptilonia magellanica* after flash chromatography followed by HPLC.

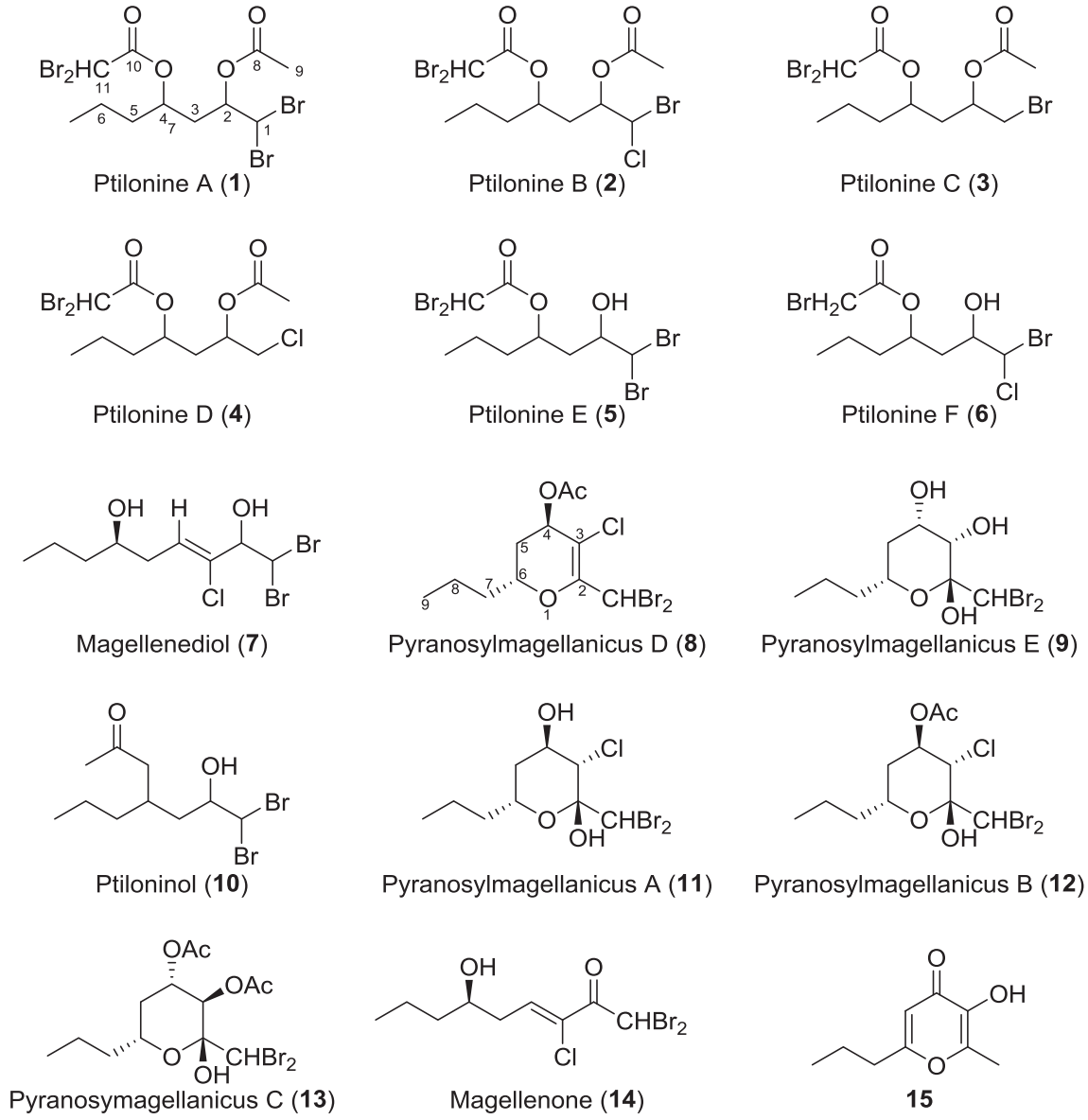

Fig. 1. Acetogenins isolated from *Ptilonia magellanica*.