Industrial Crops & Products 121 (2018) 250–257

Contents lists available at ScienceDirect

Industrial Crops & Products

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

Sea rose (*Armeria pungens* (Link) Hoffmanns. & Link) as a potential source of innovative industrial products for anti-ageing applications

Maria J. Rodrigues[a], Catarina A. Pereira[a], Marta Oliveira[a], Nuno R. Neng[b], José M.F. Nogueira[b], Gokhan Zengin[c], M. Fawzi Mahomoodally[d], Luísa Custódio[a,*]

[a] Centre of Marine Sciences, University of Algarve, Faculty of Sciences and Technology, Ed. 7, Campus of Gambelas, 8005-139 Faro, Portugal
[b] Centro de Química e Bioquímica, Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Ed. C8, 1749-016 Lisbon, Portugal
[c] Selcuk University, Science Faculty, Department of Biology, Campus, 42250, Konya, Turkey
[d] University of Mauritius, Faculty of Science, Department of Health Sciences, Réduit, Mauritius

ARTICLE INFO

Keywords:
Halophytes
Acetylcholinesterase
Antioxidant
α-Glucosidase
Tyrosinase
Elastase

ABSTRACT

This work explored for the first time the halophyte *Armeria pungens* (Link) Hoffmanns. & Link (sea rose) as a potential source of industrial natural products with anti-ageing potential. In this sense, ethyl acetate, acetone, ethanol and water extracts were prepared from flowers, peduncles and leaves of sea rose and evaluated for *in vitro* antioxidant capacity by four complementary methods and enzyme inhibitory effects towards enzymes related with the onset of different diseases, namely acetyl- (AChE) and butyrylcholinesterase (BuChE), α-glucosidase, tyrosinase, lipase and elastase. The polyphenolic composition of the extracts was appraised by high-pressure liquid chromatography coupled with diode array detection analysis (HPLC-DAD). Nineteen phenolic compounds were identified in the extracts, including flavonoids, hydroxybenzoic and hydroxycinnamic acids, and catechin was the main compound detected. The ethanol extract of sea rose leaves was the most effective as DPPH (IC_{50} = 83.7 μg/mL) and ABTS (IC_{50} = 146 μg/mL) scavenger, and also as a copper chelator (IC_{50} = 81.8 μg/mL). The acetone peduncles' extract had the highest iron chelating activity (IC_{50} = 142 μg/mL). Water and ethanol leaf extracts showed the uppermost AChE inhibition (water: IC_{50} = 87.6 μg/mL; ethanol: IC_{50} = 90.3 μg/mL). In turn, the ethanol flower extract had the lowest IC_{50} values towards α-glucosidase (26.7 μg/mL) and tyrosinase (268 μg/mL). The leaf ethanol extract had the highest capacity to inhibit elastase (IC_{50} = 531 μg/mL), while none of the extracts had significant inhibitory activity on BuChE and lipase. In conclusion, ethanol extracts from leaves and flowers of sea rose showed to be the most promising source of natural products for industrial applications, with anti-ageing properties, namely neuroprotective, anti-diabetic, anti-wrinkles and anti-melanogenic activities.

1. Introduction

Plants are considered one of the most important sources of materials for the development of novel products for pharmaceutical, cosmetic and food industries. However, halophytes species that thrive in high salinity and UV-radiation conditions, only recently have started to be explored for these purposes. The extreme conditions to which halophytes are subjected are highly toxic to the plants, inducing severe changes in their physiology such as hyper osmotic shock, photosynthesis' inhibition and nutrient imbalance (Aslam et al., 2011). However, these species evolved to counterbalance these conditions through different morphological and physiological mechanisms, such as the production of antioxidant enzymatic defence machineries, maintenance of ionic and osmotic homeostasis and synthesis of primary (e.g. sugars, phytosterols) and secondary metabolites (e.g. phenolics and alkaloids) (Ksouri et al., 2012; Zengin et al., 2018a). These metabolites have protective roles in plants and display a high range of biological properties with health promoting effects, as for example antioxidant, anti-inflammatory, neuroprotective and anti-diabetic (Rodrigues et al., 2014, 2017a, 2017b, 2018). This chemical richness may explain the traditional use of halophytes for medicinal purposes and confer them a high potential as sources of biomolecules with multiple industrial applications namely in the food, pharma and cosmetic areas (Ksouri et al., 2012; Rodrigues et al., 2014, 2017a, 2017b, 2018; Zengin et al., 2018b). Some halophytic species are already used as industrial crops, for example quinoa seeds (*Chenopodium quinoa*) have a high commercial value while *Salicornia* species are used in the food industry a fresh gourmet product and as a salt substitute (Maggio et al., 2011, Patel, 2016, Barreira et al.,

* Corresponding author.
E-mail address: lcustodio@ualg.pt (L. Custódio).

https://doi.org/10.1016/j.indcrop.2018.05.018
Received 8 March 2018; Received in revised form 4 May 2018; Accepted 7 May 2018

2017). Active ingredients or herbal extracts from other species are used in the cosmetic industry as skincare formulations, as for example *Haloxylon articulatum* (Cav.) Bunge (Jdey et al., 2017), *Armeria maritima* (Mill.) Willd. (Laloeuf, 2014), *Beta maritima* L., *Chrithmum maritimum* L. and *Limonium latifolium* Kuntze (Schaefer, 2009). In addition, specific species were described as possible sources of molecules for pharmaceutics applications, including *Juncus acutus* L. (Rodrigues et al., 2014), *Polygonum maritimum* L. (Rodrigues et al., 2017a, 2018), *Thespesia populneoides* (Roxb.) Kostel., *Salvadora persica* L., *Ipomoea pes-caprae* (L.) R.Br., *Suaeda fruticosa* (L.) Forssk. and *Pluchea lanceolata* (DC.) Oliv. & Hiern (Qasim et al., 2017).

The process of ageing is complex and results from the accumulation of various damages and pathologies in different tissues as a consequence of cellular maintenance pathways' failure (Niccoli and Partridge, 2012). The increased number of elderly persons rises the incidence of age related diseases, as for example Alzheimer's disease (AD), type 2 *diabetes mellitus* (T2DM) and obesity (Niccoli and Partridge, 2012; WHO, 2016). This drives the need for novel and more effective therapeutics to manage these diseases and to improve the quality of life of the elderly. One of the possible approaches is to target the inhibition of key enzymes linked with the progression of those health problems, that contributing to alleviate the symptoms. This is the case of the inhibition of acetyl- (AChE) and butyrylcholinesterase (BuChE) for AD, α-glucosidase for T2DM, lipase for obesity, tyrosinase for skin hyperpigmentation and elastase for skin ageing (Zengin et al., 2018a).

In view of the growing consumers' needs and preferences for natural and safer products with health promoting properties, there is a growing need to use medicinal plants for medical formulations and therapeutic purposes, such as halophyte plants. The Plumbaginaceae family comprises around 725 cosmopolitan species divided in 30 genera that are especially found on salt steppes and sea coasts (Christenhusz and Byng, 2016). This family is a valuable source of medicinal commodities, however, there is reduced information regarding the therapeutic potential of the *Armeria* genus. Still, there are reports of the use of species belonging to this genus to treat nervous system disorders, urinary infections and with slimming properties (Usher, 1974; Stuart, 1979). *Armeria maritima* (Mill.) Willd., for instance, is reported to have compounds able to enhance the skin barrier function, and to reduce the ageing effects resulting from skin dehydration, irritation and inflammation (Laloeuf, 2014). Hydroethanolic extracts from *A. pubigera* (Desf.) Boiss., *A. transmontana* (Samp.) G.H.M.Lawrence and *A. merino* (Bernis) Nieto Fel. & Silva Pando have a high phenolic content and display radical scavenging capacity, ultraviolet radiation absorption capacity, antiradical protection and stimulation of human skin fibroblast cells proliferation (Martínez et al., 2012).

Sea rose (*Armeria pungens* (Link) Hoffmanns. & Link) is an endemic species usually found in dunes and coastal sands (primary and secondary dune) of Portugal, Spain, France (Corsica) and Italy (Sardinia). Despite the medicinal uses of plants belonging to its family and genus, to the best of our knowledge, nothing is known about the chemical profile or biological activities of sea rose. In this context, this work intended to determine the *in vitro* radical scavenging, metal chelating and enzyme inhibitory properties (acetyl-, butyrylcholinesterase, tyrosinase, α-glucosidase, lipase and elastase) of ethyl acetate, acetone, ethanol and water extracts obtained from different plant parts (flowers, peduncles and leaves) from *A. pungens*. The phenolic profile of the extracts was also obtained using spectrophotometric methods and by high-performance liquid chromatography (HPLC) coupled with diode array detection (DAD) analysis.

2. Materials and methods

2.1. Chemicals

The 1,1-diphenyl-2picrylhydrazyl (DPPH), catechin, epicatechin, epigallocatechin gallate, rutin, quercetin, naringenin 7-O-glucoside, luteolin 7-O-glucoside, gallic, *p*-hydroxybenzoic, gentisic, syringic, salicylic, ellagic, chlorogenic, caffeic, ferulic, rosmarinic and coumaric acids and 4-hydroxybenzaldehyde was purchased from Sigma-Aldrich (Germany). Merck (Germany) supplied Folin-Ciocalteau (F-C) phenol reagent. Additional reagents and solvents were obtained from VWR International (Belgium).

2.2. Plant material

Samples from *A. pungens* were collected in the South of Portugal (Ancão beach) in July of 2017 (coordinates: 37°2′2.094″N 8°2′23.863″W). The taxonomical classification was confirmed by the botanist Dr. Manuel J. Pinto (National Museum of Natural History, University of Lisbon, Botanical Garden, Portugal) and a voucher specimen (voucher code: MBH38) is kept in the herbarium of the Marbiotech laboratory. Plants were divided in flowers, peduncles and leaves, oven dried for 3 days at 40 °C, powdered and stored at −20 °C until needed.

2.3. Extraction

Dried samples were separately mixed with ethyl acetate, acetone, ethanol and water (1:40 w/v), and extracted overnight at room temperature (RT, approx. 20 °C) under stirring. This procedure was repeated twice, and extracts were filtered (Whatman n° 4) and evaporated under vacuum. Dried extracts were dissolved in the corresponding solvent at the concentration of 10000 µg/mL and stored at −20 °C.

2.4. Phenolic composition

2.4.1. Determination of total phenolics (TPC), flavonoids (TFC), condensed tannins (CTC) and hydroxycinnamic acids (HCA) contents

TPC, TFC, CTC and HCA were determined in the extracts at the concentration of 1000 µg/mL and absorbance was measured in a microplate reader (Biotek Synergy 4). TPC was assessed by the F-C assay, TFC was estimated by the aluminium chloride colorimetric method adapted to 96-well microplates, CTC was evaluated by the 4-dimethylaminocinnamaldehyde-hydrochloric acid colorimetric method adapted to 96-well microplates, and HCA was estimated by the spectrophotometric methods adapted to 96-well microplates. Results were expressed respectively as gallic acid (GAE), rutin (RE), catechin (CE) and caffeic acid (CAE) equivalents in milligrams per gram of extract (dry weight, DW). All methods were performed as described in Rodrigues et al. (2015).

2.4.2. Identification and quantification of phenolic compounds by HPLC-DAD

The extracts at the concentration of 10000 µg/mL in ultrapure water were analysed by HPLC-DAD (Agilent 1100 Series LC system, Germany), as described before (Rodrigues et al., 2015). For identification, the retention parameters of each assay were compared with the standard controls and peak purity was assessed using UV–vis spectral reference data. Levels of the different compounds were extrapolated from calibration standard curves. Commercial standards (catechin, epicatechin, epigallocatechin gallate, rutin, quercetin, naringenin 7-O-glucoside, luteolin 7-O-glucoside, gallic, *p*-hydroxybenzoic, gentisic, syringic, salicylic, ellagic, chlorogenic, caffeic, ferulic, rosmarinic and coumaric acids and 4-hydroxybenzaldehyde) were prepared in methanol (10000 mg/L) and diluted with ultrapure water in the desired concentration.

2.5. Antioxidant activity

2.5.1. Radical scavenging activity (RSA) on DPPH and ABTS radicals

The RSA on the DPPH radical and ABTS radicals was evaluated as