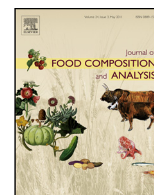
Journal of Food Composition and Analysis 39 (2015) 77–86

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

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



Original Research Article

Variation of sesquiterpene lactones and phenolics in chicory and endive germplasm

Federico Ferioli *, Manuela Agata Manco, L. Filippo D'Antuono

Department of Agri-Food Science and Technology, Food Science University Campus, University of Bologna, Piazza Goidanich 60, 47521 Cesena, Italy

ARTICLE INFO

Article history:
Received 19 August 2013
Received in revised form 21 November 2014
Accepted 21 November 2014
Available online 14 January 2015

Keywords:
Chicory
Endive
Germplasm
Sesquiterpene lactones
Phenolics
Hydroxycinnamic acids
Flavonoids
Food composition
Food analysis

ABSTRACT

Fresh edible parts of 32 endive (var. *crispum* and *latifolium*) and 64 chicory accessions (Head radicchio, Sugarloaf, Leafy radicchio, and Witloof types) were analyzed for their sesquiterpene lactone (SL) and phenolic concentrations, and HPLC profile. Six SL and 20 phenolic compounds, belonging to hydroxycinnamic acids, flavonoids, and anthocyanins, were quantified. Total SL were in the range of 128–2045 and 383–2497 mg kg^{-1} d.m. for endive and chicory, respectively, whereas total phenolics ranged from 2207 to 15,235 and from 1356 to 77,907 mg kg^{-1} d.m. in the two species. An ample variability and significant differences were detected between endive and chicory and among variety and type, within species. On average, the highest SL concentration was verified in Sugarloaf chicory, whereas red Head radicchio chicories showed the highest phenolic concentration. The two species were clearly separated on the basis of discriminant analysis, with Witloof chicory showing some similar features to endive.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Chicory (*Cichorium intybus* L.) and endive (*Cichorium endivia* L.), belonging to the *Asteraceae* family, are popular vegetables consumed in various ways and increasing amounts, since they are perceived as being "healthy" and low caloric meal components (DuPont et al., 2000). Both species include ample shape and color variability, some types being very attractive and appreciated for their texture and flavor. From a sensory and a nutritional standpoint, chicory and endive quality is primarily affected by two specific classes of compounds: sesquiterpene lactones (SL) and phenolics.

SLs, also known as "bitter principles", are C-15 terpenoid compounds, characteristic of the *Asteraceae* and also sporadically occurring in *Umbelliferae* and *Magnoliaceae* families (Merfort, 2002). SLs are responsible of chicory bitterness, and promote appetite and digestion in humans (Kisiel and Zielińska, 2001). They are interesting substances from chemical and chemotaxonomic point of view and have also been investigated for putative anti-tumor, anti-leukaemic, cytotoxic, antimicrobial activity (Price et al., 1990; Tamaki et al., 1995), as well for their allergenic properties (Malarz et al., 2002).

Different investigations were carried out to isolate and characterize the structure of SL from chicory, lettuce, and other *Asteraceae* (Kisiel and Barszcz, 1997; Kisiel and Michalska, 2008; Kisiel and Zielińska, 2001; Kisiel et al., 1997; Michalska et al., 2009). The most abundant SL identified in chicory leaves, lactucin, 8-deoxylactucin, lactucopicrin, and their saturated 11β,13-dihydroderivatives, are based on a guaiane skeleton. Some SLs are present both in the free forms and as their glycosides.

Few studies have focused on SL distribution in chicory and endive varieties (Foster et al., 2006; Price et al., 1990), or in chicory cultivars (Peters and Van Amerongen, 1996, 1998; Peters et al., 1997). In these researches SL determination was performed by means of enzyme-linked immunosorbent assay (ELISA), based on antibodies that recognize these phytochemicals and their precursors. These methods do not require any extraction and make it possible to quantify lactucin and luctucopicrin-like compounds, but not to identify and quantify individual SLs, or to discriminate between free and bound SL.

The antioxidant and radical scavenger activity of phenolic compounds is well documented (Chen and Chen, 2013; Weng and Yen, 2012). Three main classes of phenolic compounds have been identified in chicory and endive: hydroxycinnamic acids, flavonoids,

* Corresponding author. Tel.: +39 0547 338126; fax: +39 0547 382348.
E-mail address: federico.ferioli@unibo.it (F. Ferioli).

http://dx.doi.org/10.1016/j.jfca.2014.11.014
0889-1575/© 2015 Elsevier Inc. All rights reserved.

and, only in red varieties, anthocyanins (Heimler et al., 2009; Innocenti et al., 2005).

To date, an extensive survey reporting and comparing the bioactive compound distribution in commercial endive and chicory samples has not been available. The present research assessed SL and phenolic concentration in 32 accessions of endive (varieties: *crispum* and *latifolium*), and 64 accessions of chicory (types: Head radicchio, Leafy radicchio, Sugarloaf, and Witloof) grown at the same site, within a project (LeafyVeg) aimed at evaluating and characterizing leafy vegetable genetic resources for their phytochemical content.

2. Materials and methods

2.1. Samples

Seeds of 32 endive accessions (*Cichorium endivia* L.), belonging to varieties *crispum* and *latifolium*, and 54 chicory accessions (*Cichorium intybus* L.), belonging to Head radicchio, Leafy radicchio, and Sugarloaf types (Table 1) were supplied by GEVES (France) and a local seed company (Italy). The seeds were planted in a nursery (July 2009) in Sala di Cesenatico (Cesenatico, Forlì-Cesena; lat. 44.156162, long. 12.384839, alt. 7.000 m). Given the small amount of seeds, the plantlets were transplanted in open field (August 2009) in unreplicated, randomly arranged plots, represented by two rows, each 4 m long. Sampling was then randomly carried out in two parts of each row, excluding the margins. The harvest took place at commercial maturity, from mid-October to mid-December 2009. The sampling was carried out on two randomly selected traits of each row, excluding the margins. The Witloof samples were directly supplied by GEVES, where they were directly produced according to standard techniques. The fresh edible aerial part of each accession was cut in small pieces (~1–2 cm), immediately frozen at −18 °C overnight, freeze-dried and ground before bioactive extraction. Each determination was performed in duplicate. The analytical data are therefore the results of four independent measurements ($n = 4$).

2.2. Reagents and chemicals

All chemicals and solvents, unless specified, were of analytical grade and purchased from Panreac (Castellar del Vallès – Barcelona, Spain) and Sigma-Aldrich (St. Louis, MO, USA). Deionized water was obtained by an Elix 10 water purification system from Millipore (Bedford, MA, USA).

2.3. Simultaneous SL and phenolic extraction

A system allowing the simultaneous SL and phenolic extraction, and stabilizing hydrophilic anthocyanins was adopted, according to Ferioli and D'Antuono (2012). This system was more effective in SL recovery in comparison to the use of commonly adopted organic solvents. Briefly, 0.5 g of freeze-dried sample were extracted twice by 15 mL of 2% (v/v) formic acid in methanol/water 4/1 (v/v). A small aliquot of the extract (3 mL) was employed for phenolic determination, whereas the residual part was dried, subjected to nitrogen flow, recovered with methanol, and divided in two portions. One portion was used to determine free SL, whereas the second one underwent an enzymatic treatment by cellulase from *Aspergillus niger* (activity: ~0.8 units mg^{-1}) to recover glycoside-bound SL, as reported by Price et al. (1990).

2.4. Purification of SL by solid phase extraction (SPE)

Both free and total SL containing fractions were purified from phenols and interfering compounds by SPE, employing Silica cartridges, according to the method proposed by Ferioli and D'Antuono (2012). Briefly, after cartridge conditioning and equilibrating, samples were loaded and eluted with dichloromethane/ethyl acetate 3/2 (v/v). Both the loading and elution fractions were collected, dried, and recovered with methanol/water 1/1 (v/v) before HPLC analysis.

2.5. HPLC determination of SL

HPLC analyses were carried out on an HPLC apparatus from Jasco (Tokyo, Japan), equipped with two binary pumps (mod. PU-1580), an autosampler (mod. AS-2055 Plus) and a diode array UV/vis detector (mod. MD-1510, quartz flow cell, 10 mm optical path). Before injection, SL extracts were filtered in HPLC glass vials through nylon syringe filters (diameter: 13 mm; pore dimension: 0.45 μm). SL elution was carried out in gradient mode employing the following solvent system: mobile phase A: methanol/water 14/86 (v/v); mobile phase B: methanol/water 64/36 (v/v). The gradient program was: from 0 to 20 min, 100–58% A; from 20 to 30 min, 58% A; from 30 to 45 min, 58–0% A; from 45 to 50 min, 0% A; from 50 to 52 min, 0–100% A; from 52 to 62 min, 100% A as post run. The flow rate was 0.5 mL min^{-1}, and the injection volume was 20 μL. Data were processed by the software Jasco-Borwin (ver. 1.50) from Jasco. Each chromatogram was recorded at 260 nm whereas absorption spectra were recorded between 200 and 400 nm. A Luna 5 μm C18 (250 mm × 3.0 mm id, 5 μm particle size) column from Phenomenex (Torrance, CA, USA), equipped with an HPLC guard cartridge system holding cartridges Gemini C18 (4 mm × 3.0 mm) from Phenomenex was employed. The analyses were carried out at 25 °C.

2.6. HPLC determination of phenolics

Phenolic determination was performed on the same HPLC apparatus employed for SL. Before injection, 0.5 mL of the crude phenolic extract were diluted with 0.5 mL of 2% (v/v) formic acid (water solution) and filtered in HPLC glass vials through nylon syringe filters (diameter: 13 mm; pore dimension: 0.45 μm). Phenolic elution was carried out in gradient mode employing the following solvent system: mobile phase A: 5% (v/v) formic acid in methanol/water 14/86 (v/v); mobile phase B: 5% (v/v) formic acid in methanol/water 64/36 (v/v). The gradient program was: from 0 to 30 min, 100–64% A; from 30 to 31.2 min, 64–0% A; from 31.2 to 40.2 min, 0% A; from 40.2 to 41.4 min, 0–100% A; from 41.4 to 47.4 min, 100% A as post run. The flow rate was 0.5 mL min^{-1} and the injection volume was 12 μL. The absorption spectra were recorded between 200 and 600 nm. A Gemini NX C18 (150 mm × 3.0 mm id, 3 μm particle size) column from Phenomenex, equipped with an HPLC guard cartridge system holding cartridges Gemini NX C18 (4 mm × 3.0 mm) from Phenomenex was employed. The analyses were carried out at 35 °C.

2.7. SL and phenolic quantification

SL quantification was done relative to santonin (≥99.0%) used as internal standard. Other SLs herein identified were not commercially available. Phenolics were quantified by external standard mode, constructing calibration curves of four representative compounds of relevant phenolic classes: hydroxycinnamic derivatives, flavonoids and anthocyanins were quantified at 330, 350 and 520 nm, respectively, using as reference compounds caffeic and chlorogenic acid, rutin and keracyanin (cyanidin-3-O-rutinoside). Stock solutions were prepared in 2% (v/v) formic acid in methanol. Diluted solutions containing all phenolics were prepared in 2% (v/v) formic acid in methanol/water 2/3 (v/v) and analyzed by HPLC in three replications. Concentration ranges were 0.5–202.4 (nine calibration points), 0.5–200.7 (nine calibration

Download English Version:

https://daneshyari.com/en/article/7620592

Download Persian Version:

https://daneshyari.com/article/7620592

Daneshyari.com