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The impact of sesquiterpene lactones and phenolics on sensory attributes: An investigation of a curly endive and escarole germplasm collection

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ABSTRACT

In the present study, curly endive (*Cichorium endivia* L. var. *crispum*) and escarole (*Cichorium endivia* L. var. *latifolium*) accessions were investigated for their sensory characters (bitterness, astringency and herbaceous flavour) and acceptance in relation to sesquiterpene lactone and phenolic content. Different facets of the perception of these sensory traits in relation to lactones and phenolics were brought out. Lactucopicrin and kaempferol malonyl glucoside were consistently related to bitterness, astringency and herbaceous flavour perceptions. Overall acceptance was significantly and inversely related mainly to bitterness. The generic statement that sesquiterpene lactones and phenolic compounds are determinants of bitterness and other related sensory characters does not seem to be fully consistent with our data, that indicated how the balance of different compounds affects these traits individually, in a rather complex manner, with a prevailing negative impact of phenolics.

Bitter, astringent, and herbaceous perceptions were significantly affected by variety, with curly endive showing on average higher scores in comparison to escarole, with particular respect to bitterness

1. Introduction

Bitterness and astringency are sensory perceptions related to plant defense mechanisms against predators. These perceptions are determined by a series of phytochemical compounds, such as phenolics, glucosinolates and sesquiterpene lactones: high levels of these compounds can make plant foods unpalatable or negatively affect consumers' acceptance. Therefore, the lowering of their content in human foods, through breeding or processing, represents a constant trend (Drewnowski & Gomez-Carneros, 2000).

Cichorium endivia L. is a popular leafy green vegetable. It exists in two forms: var. *crispum* Lam. (curly endive) and var. *latifolium* Lam. (escarole), both appreciated for their distinctive crunchy texture and mildly bitter taste, making them suitable for direct consumption or as ingredients of mixed ready-to-eat salads. Being a member of the *Asteraceae* family, endive is characterized by the presence of sesquiterpene lactones (SL), as well as phenolic compounds.

Bitterness, the dominant taste of chicory, has been linked to the presence of SL, in particular lactucin and lactucopicrin (Peters & Van Amerongen, 1998; Poli et al., 2002; Price, DuPont, Shepherd, Chan, & Fenwick, 1990; Seo, Yang, Kays, Lee, & Park, 2009; Van Beek et al., 1990).

Phenolics are well known key determinants of bitter, astringent and pungent tastes of different foods and beverages, such as bread and crackers (Challacombe, Abdel-Aal, Seetharamana, & Duizer, 2012), chocolate (Harwood, Ziegler, & Hayes, 2013), tea (Yu, Yeo, Low, & Zhou, 2014), virgin olive oil (Bendini et al., 2007; Esti, Contini, Moneta, & Sinesio, 2009; Servili & Montedoro, 2002), and wine (Hufnagel & Hofmann, 2008).

The biological activity of SL and phenolics is not limited to their sensory impact, but involves several other functional aspects. Chicory has been investigated, in relation to SL content, for its liver-protective effects (Ahmed, Al-Howiriny, & Siddiqui, 2003; Gadgoli & Mishra, 1997), anti-diabetic properties (Kim, 2000; Pushparaj, Low, Manikandan, Tan, & Tan, 2007), as a tumor inhibitor (Hazra, Sarkar, Bhattacharyya, & Roy, 2002; Rasmussen, Zamaratskaia, & Ekstrand, 2011), and blood vessel protectant (Schumacher et al., 2011). SL are also well known as potential allergenics (Friis, Hjort, Vail, & Mitchell, 1975; Helbling, Reimers, Wälti, Borgts, & Brander, 1997; Pirson, Detry, & Pilette, 2009). The antioxidant and radical scavenging activity of phenolic compounds has been well investigated and subject of recurrent reviews (Chen & Chen, 2013; Weng & Yen, 2012), with specific evidence for the activity of chicory phenolics (Rossetto et al., 2005).

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To date, an investigation relating phytochemical levels and sensory profiles of commercial endive samples has not been available. As a part of a research line aimed at the qualitative evaluation of leafy vegetables, including endive and chicory, whose detailed chemical results have been reported elsewhere (Ferioli, Manco, & D'Antuono, 2015), the present investigation focused on the sensory characterization of 28 endive accessions, in relation to their SL and phenolic content. The main aims of this research were: (a) to add information on the impact of SL and phenolics on sensory traits, using endive as study material for the first time; (b) to explore the variability of this still lesser known germplasm; (c) to preliminarily verify the relations between sensory traits, SL and phenolics and acceptance.

2. Materials and methods

2.1. Plant material

Seeds of endive (*Cichorium endivia* L.) accessions, belonging to varieties *crispum* (curly endive) and *latifolium* (escarole) were supplied by the GEVES gene bank (Group d'étude et de contrôle des variétés et de semences, France) and a local seed company (Italy). Information about sowing and sampling procedures, accession names and working tags (the same herein employed), is given in the study by Ferioli et al. (2015).

The samples were harvested between mid-October and mid-December, according to their commercial maturity, assessed as the compactness of the heads. For chemical analyses, 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 SL and phenolic extraction.

2.2. Sensory analysis

2.2.1. Panel selection and training

Twelve people, usually attending as panelists at sensory evaluation sessions, were recruited among personnel of our research laboratory, on the basis of their availability to attend all sessions of training and subsequent evaluation sessions.

The first training started with a brain storming session, during which different commercial samples of chicory and endive were tested for visual, olfactory and gustative traits, with the aim of finding an agreement about the relevant sensory characters to be evaluated. At the end, a consensus was found on three basic gustative and olfactory characters: bitterness, astringency, and herbaceous flavour.

In a second session, the capacity of panelists to recognize these traits was assessed. The following solutions were prepared: bitter (caffeine in water; concentrations: 0.025, 0.125, 0.250, 0.500 g l^{-1}), astringent (tannin in water; concentrations: 0.1, 0.2, 0.4, 1.0, 2.0 g l^{-1}) and herbaceous aroma (a filtrate of a blend of 8 pea pods in 250 ml water; concentrations: 20, 50, 100, 250, 500 ml l^{-1}). At each corresponding dilution of the scale, the panelists were asked to recognize the three sensory characters. This test was not replicated.

Finally, the panelists were asked to correctly rank the different dilutions of the three solutions, including a pure water blank, with two replications.

At the end, eight panelists were retained for quantitative sensory evaluations.

2.2.2. Sensory and hedonic evaluations

For sensory analysis, the heads were washed and stored in a refrigerator until the day after harvest. The individual accessions were served shredded on plastic plates, and labelled with three digit random numbers. At each session, four to six samples were evaluated, according to the number of samples harvested. The sensory profiling was carried out using a 9 point scale, with end-point anchor words: "nor perceived" and "very intense".

Although true sense formal consumer analysis was not within the scopes of this research, a preliminary attempt to relate sensory traits, as determined by SL and phenolics, to acceptance was carried out. For this reason, hedonic overall acceptance was independently rated by 24 assessors, recruited on a free participation basis, the same days of quantitative profiling. A nine-point scale was used also in this case, with end point anchor words "dislike a lot" and "like a lot".

2.3. Chemical analyses

SL and phenolic extraction and successive analyses were carried out following the procedure illustrated in detail by Ferioli and D'Antuono (2012) and Ferioli et al. (2015), and hereafter shortly summarized.

2.3.1. Extraction of SL and phenolic compounds

Briefly, 0.5 g of freeze-dried material were extracted by 2% (v/v) formic acid in methanol/water 4/1 (v/v). An aliquot of the extract was employed for phenolic determination, whereas the residual part was used to determine free and, after enzymatic treatment by cellulase enzyme, total SL.

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

Before HPLC determination, extracts containing free and total SL were purified from phenolics and other interfering compounds by SPE, employing silica-based cartridges. 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 in methanol/water 1/1 (v/v).

2.3.3. HPLC operating conditions

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, free SL, total SL, and phenolic containing extracts were filtered in HPLC glass vials through nylon syringe filters (diameter: 13 mm; pore dimension: 0.45 mm).

2.3.4. SL and phenolic quantification

SL were quantified using santonin as internal standard, whereas phenolic amount was determined by external standard mode, constructing calibration curves of representative compounds of major phenolic classes: caffeic and chlorogenic acid for hydroxycinnamic acid quantification, and rutin for flavonoid quantification.

2.3.5. SL and phenolic identification

SL and phenolics were identified by a liquid chromatography system HP 1100 Series coupled with a mass detector (mod. G1946A) both from Agilent Technologies (Palo Alto, CA, USA). The mass spectrometer operated both in positive and negative atmospheric pressure ionization-electro-spray source (API-ES) mode.

2.4. Data analysis

Two way analysis of variance was carried out on the three descriptive characters and hedonic ratings, using accessions and panelists as effects, without an interaction term. Differences among samples were detected by means of Protected Least Square