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QUANTITATIVE ANALYSIS OF SOME CLASSES OF BIOACTIVE ANTIOXIDANT COMPOUNDS IN CARAWAY (CARUM CARVI L.) LEAVES

Pricop Simona-Mariana, Popoviciu Dan Răzvan* "Ovidius" University of Constanța, Faculty of Natural Sciences and Agricultural Sciences, Constanta, Romania

* Correspondence author. E-mail: dr_popoviciu@yahoo.com

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ABSTRACT

Caraway leaves from local production were studied for their content in some classes of compounds with antioxidant potential. Chlorophylls, carotenoids (total, β-carotene, lycopene, lutein, zeaxanthin and cryptoxanthin), phenolic compounds (total, flavonoids, anthocyanins), ascorbic acid, essential oils.

The chlorophyll content was 346 mg/kg DW, of which only chlorophyll a was found in detectable amounts. Total carotenoid concentration was 2,190 mg/kg DW, consisting almost entirely (2,078 mg/kg) of β -carotene including, 86 mg/kg lutein and low amounts of other compounds. 23,755 mg/kg was the total phenolic content, of which 6,435 mg/kg flavonoids, including 104 mg/kg anthocyanins. Leaves contained 2,319 mg/kg ascorbic acid and 6,676 mg/kg essential oil.

These concentrations are comparable with those commonly found in most studied species of Apiaceae.

INTRODUCTION

Caraway (*Carum carvi* L., Apiaceae family) is a herbaceous aromatic plant, native of Western Eurasia and North Africa. It has a medium-sized (30-100 cm) stem, a fleshy taproot, long (20-30 cm), narrow, pinnately dissected leaves, white, pink or reddish flowers grouped in compound umbels. Fruits are indehiscent schizocarps.

It is widely cultivated as an aromatic and medicinal plant and, in the last years it is gaining popularity in Romania also. While leaves are known to be aromatic, the main part used is the fruit, used under their natural form, dried and ground or as extracted oil. Usage is variate, including cuisine, bakery, beverage production, cosmetics and folk medicine or pharmacy.

Among its medicinal uses, it is known to be antioxidant, antimicrobial, vermicidal, anti-carcinogenic, diuretic, immuno-modulatory, hepatotonic, galactopoietic, and antispasmodic (Sachan et al. 2016, Naquibuddin et al. 2021).

Plants are known to contain several classes of bioactive compounds with antioxidant potential.

Chlorophylls (of which chlorophylls a and b are found in land plants) are the main pigments used in photosynthesis. They also have anti-inflammatory activity for consumers, enhance wound healing and inhibit calcium oxalate dihydrate accumulation (kidney stones), while limiting dietary uptake of some known carcinogens. Chlorophylls are among the main antioxidant compounds, preventing oxidative stress-associated diseases (Inanç 2011).

Carotenoids (including carotenes, lutein, lycopene, zeaxanthin) are accessory photosynthetic pigments. Some of them (especially carotene) are precursors of retinol and key to melanin synthesis, thus important for eye and skin functioning. They are also antioxidant and antiproliferative and researches show that lycopene is among the most important dietary anticarcinogens (Eldahshan & Singab 2013).

Phenolic compounds are a variate group of bioactive compounds, functioning as plant pigments, but also as antimicrobials and antifungals. Flavonoids (among them being anthocyanins – plant pigments and strong antioxidants), phenolic acids and tannins belong to this group (Kivrak & Kivrak 2014). For consumers, phenolic compounds are a key class of antioxidant, reducing and radical scavenging agents (Zymonė et al. 2018).

Ascorbic acid (vitamin C) is a key antioxidant, countering lipid oxidation at cell level in all organisms (Riscahyani et al. 2019)

Essential oils are complex mixtures of organic compounds, of which over 90% are volatile. Their composition includes terpenes (mostly mono- and sesquiterpenes), hydrocarbons and derivatives, flavonoids, aldehydes, alcohols, esters, etc., with a volatile fraction over 90%. They give plant products their specific aroma, while also having antimicrobial and antioxidant properties (Orphanides et al. 2011).

The objective of this paper was to determine the amount of several compounds and compound classes belonging to these categories in fennel leaves.

MATERIAL AND METHODS

Caraway leaves were collected from the experimental farm of the "Ovidius" University of Constanta.

Chlorophylls and carotenoids were determined by 80% acetone extraction and spectrophotometric absorption reading (S106 WPA spectrophotometer) at 470, 647, 663 nm (Popoviciu et al. 2020). Concentrations were calculated according to Lichtenthaler & Buschmann 2001.

Among individual carotenoid compounds, β -carotene, lycopene, lutein (and lutein esters), zeaxanthin and cryptoxanthin were determined by extraction in acetone:hexane:petroleum ether, petroleum ether, ethanol, acetone and using the spectrophotometric methods of Braniša et al. 2014, Sujith et al. 2010, Butnariu et al. 2014, Biehler et al. 2010, respectively.

The total concentration of phenolic compounds was determined by extracting plant tissue in methanol and reaction with Folin-Ciocâlteu reagent (10%) and sodium bicarbonate (7.5%) for 30 minutes. Absorbance was read at 765 nm against gallic acid calibration curve (Popoviciu et al. 2020). Flavonoids were determined by precipitation with hydrochloric acid and formaldehyde, followed by quantification of non-flavonoid phenolic content by Folin-Ciocâlteu reaction (de Lima et al. 2011). Anthocyanins were determined by 70% ethanol extraction and spectrophotometry at 520 and 700 nm (Braniša et al. 2014).

For total ascorbic and dehydroascorbic acid, ethanol extraction, reaction with ammonium molybdate and sulfuric acid, followed by spectrophotometric reading at 494 nm were employed (Riscahyani et al. 2019)

Essential oils were determined by petroleum ether extraction and gravimetry (Orphanides et al. 2011).

Dry biomass (22.33% on average) was determined through oven drying and used to express the concentrations of bioactive compounds in mg/kg DW.

RESULTS AND DISCUSSIONS

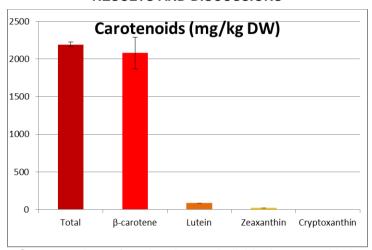


Figure 1. Concentrations of total and some individual carotenoids in caraway leaves (mg/kg DW).

The concentrations of various classes of compounds with bioactive potential are shown in Figures 1-4.

Total chlorophyll content was 346 mg/kg, all consisting of chlorophyll a, since chlorophyll b concentrations were below detection limit.

Carotenoids were 2,190 mg/kg. Of this amount, β -carotene constituted 95% (2,078 mg/kg). Lycopene amounts were below detection limits. Lutein was the second carotenoid compound, with 86 mg/kg (3.92% of the total amount). Xanthins were found in low amounts: zeaxanthin 22 mg/kg (below 1%) and cryptoxanthin 4.73 mg/kg. Apiaceae leaves are known to be a rich source of carotenoids, of which β -carotene is usually dominant. Researches on anise, chervil and dill found amounts of 126-179 mg/kg FW of this compound, lower than the 374 mg/kg FW equivalent found in caraway. Just like in our findings these species also contain mostly β -carotene, with significant amounts of lutein (9-18 mg/kg FW compared to 19.19 mg/kg; Giordano et al. 2022). On the other hand, it should be noted that carotenoid content is a highly variable character, that can show major differences among cultivars of the same species, as shown in coriander (from 15 to 103 mg/kg β -carotene; Priyadarshi & Naidu 2019).

Average total phenolic content was 23,755 mg/kg. Of these, the flavonoid fraction constituted 27% (6,435 mg/kg). Of flavonoids, a small fraction of 1.6% (104 mg/kg) were anthocyanin pigments. For comparison, other phenolic contents found in Apiaceae leaves range from 2,300 (cumin) to 21,630 (parsley) mg/kg DW. However, in most cases flavonoids constitute 50% or higher (Deroiuch 2020; Pricop et al. 2020; Thiviya et al. 2021).

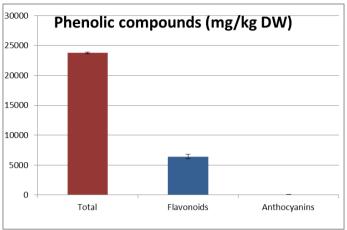


Figure 2. Concentrations of total phenolic compounds, flavonoids and anthocyanins in caraway leaves (mg/kg DW)

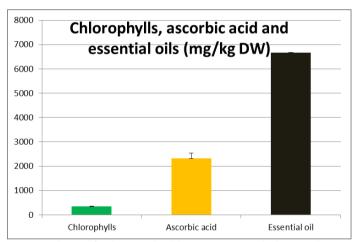


Figure 3. Concentrations of other antioxidant compound classes in caraway leaves (mg/kg DW).

2,319 mg/kg was the total amount of ascorbic and dehydroascorbic acid, while the average concentration of volatile oils was 6,676 mg/kg. The amount of ascorbic acid (518 mg/kg FW), while high, is lower than those found in other Apiaceae, like chervil and dill (Giordano et al. 2022).

CONCLUSIONS

Caraway leaves had a significant chlorophyll content (346 mg/kg DW), mostly chlorophyll a.

With 2,190 mg/kg DW, the carotenoid concentration was also high, dominated by $\beta\text{-carotene}$ constituted over 95% (2,078 mg/kg). No lycopene was found, but lutein content was similar to that other related species (86 mg/kg DW), while also hosting a significant amount of zeaxanthin (22 mg/kg DW).

At 23,755 mg/kg DW, the total phenolic inventory is comparable or higher than that found in other Apiaceae. While rich in total phenols, fennel leaves had a moderate amount of flavonoids (6,435 mg/kg), of which below 2% were anthocyanins.

Average ascorbic acid content was 2,319 mg/kg, comparable, but lower than in other Apiaceae species.

Caraway leaves were also rich in essential oils, with an average concentration of 6,676 mg/kg DW.

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