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Silphium L. extracts – composition and protective effect on fatty acids content in sunflower oil subjected to heating and storage

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ABSTRACT

The influence of ethanol and hexane extracts from leaves, inflorescences, and rhizomes of *Silphium perfoliatum, Silphium trifoliatum, Silphium integrifolium* on fatty acid content changes in sunflower oil subjected to heating and storage was studied in comparison to the synthetic antioxidant – butylated hydroxyanisole (BHA). A positive effect of extracts made of above-ground and underground organs of *Silphium* on the durable quantitative composition of fatty acids was proven. Tested extracts elevated the value of change inhibition with reference to linoleic acid to a level comparable with BHA, and sometimes, in appropriate systems, they were characterized by better values (for oil stored for 180 days at room temperature, the inhibition coefficient for linoleic acid changes reached 4.6% for 0.04% BHA, and 7.09% for hexane extract made of *S. trifoliatum* inflorescences, 400 μl/2 g; for oil heated for 120 h, the inhibition coefficient of linoleic acid changes amounted to 11.32% for 0.06% BHA, and 15.69% for hexane extract made of *S. perfoliatum* rhizomes, 600 μl/2 g). It was found that active substances groups such as phenolic acids, flavonoids and terpenes were present in tested extracts.

1. Introduction

The application of food processing considerably affects the nutritional value of fats. During thermal processing, hydrolysis, oxidation, and polymerisation of fats occur, which leads to the formation of dimers and polymers, as well as cyclic monomers and fatty acids of unidentified structure. Those compounds show toxic effects to human and animal organisms (Berdeaux et al., 2007; Erhan, Sheng, & Hwang, 2003; Korus & Mousetis, 1984; Seppanen & Csallany, 2006; Tolvanen et al., 2007; Ziemlański, 1997). Therefore, it is important to search for safe synthetic substances as well as natural ones that would protect stored and thermally processed fat. Mixtures of natural substances present in herb extracts are extremely interesting in that respect (Farag, El-Baroty, & Basuny, 2003; Frankel, 1993; Marinova & Yanishlieva, 1996; Zia-ur-Rehman, Salaria, & Habib, 2003; Frutos & Hernández-Herrero, 2005; Shyamala, Gupta, Lakshmi, & Prakash, 2005). Proper concentrations of those agents may reduce lipid oxidation or delay that process without posing a threat to the human organism. Moreover, addition of natural substances may enrich food in biologically active components and impart to it functional or medical properties (Oberdieck, 2004; Kowalski, 2007c).

Besides commonly utilized plants, also those forgotten and poorly studied that had been once used by people seem to be very promising. Plants of genus *Silphium* L. that are perennials from Asteraceae family (sub-family Asteroideae, tribe Heliantheae) are an interesting group of species. They can be found in prairies, fields, open forests, and shrubberies in middle and eastern parts of USA and Canada. It is worth mentioning that North-American Indian tribes applied various organs of *Silphium perfoliatum* L. for medical purposes (Herrick, 1977). The root of *S. perfoliatum* has tonic, diaphoretic, and alterative properties. It was found useful in liver and spleen maladies, also in treatment of fevers, internal bruises, debility, and ulcers. American Indians from the Fox tribe recommended the use of *Silphium integrifolium* rhizomes for treatment in kidney diseases and as an analgesic agent, and used a brew prepared from its leaves in the treatment of urinary bladder disturbances (Smith, 1928). Studies carried out on the biological activity of extracts from *S. perfoliatum* indicate its abilities in healing acceleration (Kujanceva & Davidjanc, 1988), and its anti-sclerotic (Syrov, Chušbaktova, & Davidjanc, 1992), and anti-fungal (Davidjanc, Kartaševa, & Nešin, 1997) properties. Kowalski and Kędzia (2007) found that methanolic and hexane extracts of *S. perfoliatum* were characterized by antibacterial action towards Gram-positive (*Enterococcus faecalis*, *Staphylococcus aureus*) and Gram-negative bacteria (*Escherichia coli, Pseudomonas aeruginosa*).

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Chemical composition determinations revealed that the above *Silphium* species contained phenolic acids (Kowalski & Wolski, 2003; Kowalski, 2004b, 2007b), flavonoids (El-Sayed et al., 2002; Kowalski, 2004b, 2007b), terpenes (Bohlmann & Jakupovic, 1979, 1980; Pcolinski, Doskotch, Lee, & Clardy, 1994) including triterpene saponins – oleanosides (Davidjanc & Abubakirov, 1992; Kowalski, 2004b, 2007a, 2007b), as well as essential oils (Kowalski, Wiercińs-ki, & Mardarowicz, 2005; Kowalski & Wolski, 2005). Moreover, rhizomes and roots of *Silphium* contained the reserve carbohydrate – inulin (Kowalski & Wierciński, 2004a), and its seeds may be an alternative source that would enrich functional food in nutrients and pro-health components (Kowalski & Wierciński, 2004b). There are also numerous publications dealing with the utilization of *S. perfoliatum* as a fodder (Duranti, Santilocchi, & Casoli, 1988).

The above data on the chemical composition of *Silphium* and biological activity of its extracts made the authors undertake studies on the opportunities of practical application of those extracts as stabilizers of stored or thermally processed fats. Therefore, the study presented in this paper was aimed at studying the influence of ethanol and hexane extracts made of leaves, inflorescences, and rhizomes of *Silphium perfoliatum*, *S. trifoliatum*, *S. integrifolium* on fatty acid content changes in sunflower oil subjected to heating and storage in comparison to a synthetic antioxidant – butylated hydroxyanisole (BHA).

2. Materials and methods

2.1. Plant materials

The leaves, inflorescences, rhizomes and roots of *S. perfoliatum*, *S. trifoliatum* and *S. integrifolium* originated from three-year-old experimental cultivation (2003) conducted by the Department of Analysis and Evaluation of Food Quality, University of Agriculture (Lublin, Poland) in Kazimierzówka near Lublin (51°14′N 22°34′E, altitude 200 m), on a lessive soil developed from loess forms on lime marl containing 1.6% of organic matter (Kowalski, 2007a). Morphological traits of the species were described in earlier papers (Kowalski & Wolski, 2001; Kowalski, 2004a, 2007b). Fresh material was frozen and then lyophilized (Labconco lyophilizer) with subsequent grinding.

2.2. Fat

Sunflower oil "Bartek" (Zakłady Przemysłu Tłuszczowego w Warszawie S.A.) purchased in a supermarket in Lublin was the study material.

2.3. Extraction

Samples of 10.00 g of lyophilized and ground plant material was weighed and transferred into conical flasks with 100 cm^3 of hexane or ethanol. Samples were then shaken for 24 h, and achieved extracts were filtered by filter paper, properly protected and stored in a fridge (+4 °C).

2.4. Chemical characteristics of extracts

2.4.1. Triterpene fraction analysis

Triterpene glycosides isolated from alcoholic extracts were hydrolysed and silanized, and then determined according to previously described procedures (Kowalski, 2007a).

2.4.2. Analysis of phenolic compounds of o-dihydroxophenol type

Determinations of phenolic compounds (with conversion for caffeic acid) were made by spectrophotometric means according to a modified Singelton and Rossi method (1965).

2.4.3. Flavonoid analysis

Determination of flavonoid content (flavonoles converted for quercetine) was performed by means of spectrophotometry according to a modified Polish Pharmacopoeia VI (2002) procedure.

2.4.4. Fatty acids analysis

About 1.000 g samples of leaf, inflorescence, and rhizomes extracts made of *S. perofliatum*, *S. integrifolium*, and *S. trifoliatum* were weighed into glass ampules (20 ml capacity). A volume of 0.1 ml of hexane solution of internal standard (heptadecanoic acid-10 mg/ml) was added to the extract (Kowalski, 2007c). Fat saponification and fatty acid esterification were performed in accordance to previously described procedures (Kowalski, 2007c).

2.4.5. GC analysis of extracts composition

Aliquots of 2 ml of extracts were taken and filtered through TFE filters (0.2 μm), then 1 ml of filtrate was transferred to vials closed with a TFE stopper and 1 ml of cholesterol solution was added (1 mg/ml). Such prepared samples were subjected to GC–MS and GC–FID determinations. Qualitative analysis was carried out on the basis of retention indices by comparing achieved spectra for separated substances with corresponding standards and literature data (Joulain & König, 1998; Adams, 2001; NIST Mass Spectral Library, 2002; Kowalski, 2005; Kowalski et al., 2005; Kowalski & Wolski, 2005). The quantitative analysis was performed on the basis of calibration curves for cholesterol, α-amyrine, β-amyrine and alkanes (C_{10}–C_{30}) within the concentration range of 0.5–400 μg/ml.

2.5. Mixtures of oils with Silphium extracts and BHA

Aliquots of 1.000 g of studied oil were introduced into glass tubes (in three replications), and then 0.2 ml, 0.4 ml, and 0.6 ml of *Silphium* extracts, ethanolic solution of BHA (2 mg/ml), and pure solvents (control) were added (Table 1). Samples were shaken to achieve emulsion and remained at ambient temperature for 24 h. Then, 1.000 g of oil was added into each tube to reach a total sample weight of 2.000 g, and stirred (Kowalski, 2007c). Such prepared samples were placed in the thermostat at 90 °C (darkness) and at room temperature (daylight). A control, i.e. samples without *Silphium* extracts and BHA, was prepared for every series.

2.6. Collection of material for study

Samples were collected after 120 h of thermostating and after 180 days of storage at room temperature. About 100 mg of oil was weighed (in three replications) into glass vials (20 ml) and 0.4 ml of internal standard solution was added – heptadecanoic acid (10 mg/ml) (Kowalski, 2007c). Then samples were subjected to saponification, esterification, and chromatographic determination in accordance to previously described procedures (Kowalski, 2007c).

Table 1
Designation of the samples

Sample	Designation
Raw oil	0
Oil with added extract 0.2 ml	200
Oil with added extract 0.4 ml	400
Oil with added extract 0.6 ml	600
Oil with added 0.2 ml BHA	BHA 200
Oil with added 0.4 ml BHA	BHA 400
Oil with added 0.6 ml BHA	BHA 600
Control	K