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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

2.7. GC analysis

2.7.1. GC–MS (analysis of triterpene fraction)

GC–MS: ITMS Varian 4000 GC–MS/MS (Varian, USA) equipped with a CP-8410 auto-injector and a 30 m × 0.25 mm VF-5 ms column (Varian, USA), film thickness 0.25 m, carrier gas He 2.5 ml/min, injector and detector temperature were, respectively, at 280 and 180 °C; split ratio 1:10; injection volume 1 l. A temperature gradient was applied (240 °C for 1 min, then incremented by 20 °C/min to 320 °C); ionization energy 70 eV; mass range: 100–870 Da; scan time 0.80 s.

2.7.2. GC–MS (analysis of components in Silphium extracts)

ITMS Varian 4000 GC–MS/MS (Varian, USA) equipped with a CP-8410 auto-injector and a 30 m × 0.25 mm VF-5 ms column (Varian, USA), film thickness 0.25 m, carrier gas He 0.5 ml/min, injector and detector temperature were, respectively, at 250 and 200 °C; split ratio 1:50; injection volume 1 μl. A temperature gradient was applied (50 °C for 1 min, then incremented by 4 °C/min to 250 °C, 250 °C for 10 min); ionization energy 70 eV; mass range: 40–350 Da; scan time 0.80 s.

2.7.3. GC–FID (analysis of components in Silphium extracts)

GC Varian 3800 (Varian, USA) equipped with a CP-8410 auto-injector and a 30 m × 0.25 mm DB-5 column (J&W Scientific, USA), film thickness 0.25 m, carrier gas He 0.5 ml/min, injector and detector FID temperatures were, respectively, at 250 and 260 °C; split ratio 1:50; injection volume 1 μl. A temperature gradient was applied (50 °C for 1 min, then incremented by 4 °C/min to 250 °C, 250 °C for 10 min).

2.7.4. GC–FID (analysis of fatty acids methyl esters)

GC was performed with Unicam 610 Series gas chromatograph equipped with a flame-ionization detector and a 60 m (0.25 mm i.d.) column coated with 0.25 μm film of HP-23. A temperature gradient was applied (160 °C for 1 min, then incremented by 2.75 °C/min to 215 °C, 215 °C for 2 min, then incremented by 40 °C/min to 230 °C, 230 °C for 2 min). The injection port and detector temperatures were 270 °C; split ratio 1:50. Hydrogen was used as carrier gas at a flow rate of 43 m/s. The quantitative analysis was performed on the basis of calibration curves for FAMES standard mixture (C14–C20) within the concentration range of 0.1–80.0 g/100 g.

2.8. Determination of extracts activity

Activity of studied extracts in experimental systems was determined on the basis of calculated inhibition I_h for quantitative changes of linoleic acid "C18:2" (Kowalski, 2007c).

$$I_{h18:2} = \left(\frac{C_{e18:2}}{C_{k18:2}} * 100\%\right) - 100\%$$

where

- $I_{h18:2}$ – inhibition of quantitative changes of linoleic acid,
- $C_{e18:2}$ – linoleic acid concentration in sample with extract addition,
- $C_{k18:2}$ – linoleic acid concentration in control sample without extract addition.

2.9. Mathematical computations

Mean values and standard deviations for quantitative results from analyses were calculated using Excel MS Office software.

3. Results and discussion

The chemical composition of *Silphium* extracts added to the sunflower oil was characterized in the experiments (Table 2–6). Alcoholic extracts made of *S. trifoliatum* and *S. integrifolium* inflorescences contained the largest amounts of glycoside-bonded oleanolic acid at levels of 2.04 and 1.59 mg/ml, while the extract prepared from *S. perfoliatum* inflorescences contained 0.28 mg/ml (Table 2). Extract made of *S. perfoliatum* rhizomes was characterized by the lowest concentration of bonded oleanolic acid (0.19 mg/ml). Moreover, ethanol extracts from *Silphium* contained glycoside-bonded ursolic acid, the highest concentration of which was recorded in leaf extracts – from 1.08 mg/ml in extract from *S. perfoliatum* to 1.32 mg/ml in extracts from *S. trifoliatum*. Extracts made of rhizomes contained only trace amounts of the ursolic acid.

Among phenolic-type substances, the concentration of o-dihydroxyphenols converted to caffeic acid (Table 2) and flavonoids contents converted to quercetin (Table 2) were determined in ethanol *Silphium* extracts. It was found that extracts made of *S. trifoliatum* leaves contained the highest level of o-dihydroxophenols (1.52 mg/ml), whereas the lowest content was recorded in extracts from *S. trifoliatum* rhizomes (0.92 mg/ml) and *S. integrifolium* rhizomes (0.61 mg/ml). Flavonoids concentrations were at the level of 0.30 mg/ml in extracts from *S. perfoliatum* leaves as well as 0.24 mg/ml and 0.25 mg/ml in extracts made of *S. trifoliatum* and *S. integrifolium* leaves, respectively. The extracts from rhizomes contained those compounds at trace concentrations. Earlier studies revealed that caffeic acid that occurs in its free and bonded forms is the main phenolic acid in the phenolic fraction prepared from *Silphium* genus (Kowalski & Wolski, 2003; Kowalski, 2004b, 2007b). Other phenolic acids identified in *Silphium* are: p-coumaric ferulic protocatechuic, p-hydroxobenzoic, vanillic, salicylic, and chlorogenic (Kowalski & Wolski, 2003; Kowalski, 2004b, 2007b). Caempherol and quercetin occurring as dominating glycoside forms were identified in the flavonoic fraction of *Silphium* (El-Sayed et al., 2002; Kowalski, 2004b, 2007b).

In present experiments, GC–MS analysis of extracts made of leaves and inflorescences of three *Silphium* species revealed qualitative similarity of these extracts (Tables 3 and 4). α-Pinene dominated among volatile constituents in ethanol and hexane extracts (44.0 μg/ml and 32.0 μg/ml), while bornyl acetate occurred only in extracts from *S. integrifolium*. Caryophyllene oxide concentration was at the level of 193.3 μg/ml in ethanol extracts from inflorescences, and 208.2 μg/ml in hexane ones. Composition of extracts produced from rhizomes (Table 5) was quite different than that from *Silphium* leaves and inflorescences, because α-pinene, α-copaene, ambroxide, and camphene occurred in trace concentrations or they were absent. Rhizome extracts were characterized by the presence of: 7-α-H-silfiperfol-5-ene, 7-β-H-silfiperfol-5-ene, and α-isocomene. Essential oils that can be easily extracted using hexane and ethanol, and isolated from *Silphium* organs, had similar chemical composition (Kowalski & Wolski, 2005; Kowalski et al., 2005). α and β amyrine (triterpene alcohols) were also present in each of the extracts used in the experiment – from 28.0 μg/ml in hexane extracts from *S. trifoliatum* rhizomes to 940.5 μg/ml in ethanol extracts from *S. perfoliatum* inflorescences. Amyrines are transitional products on the course of oleanolic and ursolic acids synthesis as well as corresponding saponins that are glycosides of these acids. Moreover, these compounds are characteristic for plants producing resins and milky juice (Kowalski, 2005).

Examined extracts did not contain significant quantities of fatty acids (Table 6), which indicates that their addition to sunflower oil should not elevate fatty acids contents in studied experimental combinations.

Table 2
Content of triterpene aglycones, o-dihydroxyphenol type phenolic compounds (converted to caffeic acid), flavonoids (flavonoles converted to quercetine) in *Silphium* ethanol extracts

Extract		Oleanolic acid	Ursolic acid	Phenolic acids	Flavonoids
Species	Organs	[mg/ml]			
S. perfoliatum	Leaves	1.25 ± 0.05	1.08 ± 0.05	1.07 ± 0.00	0.30 ± 0.00
	Inflorescences	0.28 ± 0.01	[A]	1.12 ± 0.00	0.10 ± 0.00
	Rhizomes	0.19 ± 0.00	[A]	1.12 ± 0.01	[B]
S. trifoliatum	Leaves	1.11 ± 0.04	1.32 ± 0.10	1.52 ± 0.07	0.24 ± 0.02
	Inflorescences	2.04 ± 0.09	0.34 ± 0.02	1.13 ± 0.02	0.12 ± 0.00
	Rhizomes	0.47 ± 0.02	0.02 ± 0.00	0.92 ± 0.05	[B]
S. integrifolium	Leaves	0.49 ± 0.03	1.21 ± 0.07	1.15 ± 0.04	0.25 ± 0.00
	Inflorescences	1.59 ± 0.07	0.39 ± 0.02	1.21 ± 0.04	0.11 ± 0.00
	Rhizomes	1.32 ± 0.07	0.19 ± 0.01	0.61 ± 0.02	0.09 ± 0.00

[A] Below detection limit – 0.01 mg/ml.
[B] Below detection limit – 0.05 mg/ml.

Table 3
Concentrations of particular components in hexane (HEX) and ethanol (ET) extracts made of *Silphium* leaves

No.	Compound	Retention index	Concentration (g/ml)					
			S. perfoliatum		*S. trifoliatum*		*S. integrifolium*	
			HEX	ET	HEX	ET	HEX	ET
1	α-Pinene	938	19.3 ± 0.6	9.0 ± 0.4	9.0 ± 0.5	5.6 ± 0.2	10.2 ± 0.5	9.3 ± 0.2
2	Camphene	949	4.6 ± 0.2	*	*	*	4.5 ± 0.3	4.3 ± 0.2
3	β-Pinene	975	3.7 ± 0.2	*	*	*	*	*
4	Limonene	1031	–	–	–	–	*	*
5	Trans-verbenol	1148	–	–	–	–	*	*
6	Verbenone	1217	*	*	–	–	*	*
7	Bornyl acetate	1286	–	–	–	–	*	*
8	7-α-H-Silphiperfol-5-ene	1320	*	–	*	–	*	*
9	α-Cubebene	1341	–	–	6.4 ± 0.4	*	–	–
10	α-Ylangene	1368	–	–	–	–	10.7 ± 0.5	*
11	α-Copaene	1375	0.2 ± 0.0	*	0.3 ± 0.0	*	0.2 ± 0.0	*
12	β-Bourbonene	1380	16.5 ± 0.4	*	4.6 ± 0.3	*	14.0 ± 0.4	*
13	β-Cubebene	1382	6.9 ± 0.2	*	2.2 ± 0.2	*	4.2 ± 0.2	*
14	(E)-Caryophyllene	1420	16.5 ± 0.4	47.8 ± 1.3	74.0 ± 1.0	135.6 ± 2.1	37.2 ± 0.6	45.2 ± 1.2
15	β-Copaene	1424	34.0 ± 0.8	*	4.7 ± 0.1	*	13.6 ± 0.5	*
16	Trans-α-bergamotene	1430	12.5 ± 0.6	*	3.5 ± 0.4	*	10.0 ± 0.3	*
17	α-Humulene	1455	13.1 ± 0.4	16.2 ± 0.4	38.0 ± 0.5	52.3 ± 1.1	12.8 ± 0.5	13.9 ± 0.5
18	γ-Muurolene	1470	25.7 ± 0.8	*	2.8 ± 0.3	*	16.5 ± 0.7	*
19	α-Amorphene	1475	33.5 ± 0.8	*	–	–	–	–
20	γ-Amorphene	1478	46.5 ± 1.1	*	–	–	–	–
21	Germacrene D	1480	16.7 ± 0.3	20.9 ± 0.7	46.9 ± 0.7	69.1 ± 1.6	480.2 ± 4.1	487.4 ± 7.9
22	Allo-aromadendr-9-ene	1490	–	–	–	–	5.7 ± 0.3	5.9 ± 0.3
23	γ-Elemene	1490	–	–	4.4 ± 0.3	*	–	–
24	Bicyclogermacrene	1495	–	–	–	–	5.3 ± 0.3	*
25	δ-Amorphene	1513	12.3 ± 0.5	*	3.8 ± 0.2	*	15.1 ± 0.5	*
26	γ-Cadinene	1515	9.5 ± 0.4	*	*	*	8.5 ± 0.3	1.3 ± 0.1
27	(E)-Nerolidol	1560	*	*	35.2 ± 0.6	29.7 ± 0.4	*	*
28	Spathulenol	1578	62.7 ± 1.0	56.5 ± 0.9	18.9 ± 0.4	13.5 ± 0.3	25.3 ± 0.7	23.7 ± 0.5
29	Caryophyllene oxide	1582	92.1 ± 0.9	128.1 ± 2.0	68.0 ± 1.0	96.1 ± 1.1	25.5 ± 0.5	28.0 ± 0.8
30	Salvial-4(14)-en-1-one	1596	3.5 ± 0.3	110.1 ± 1.1	3.1 ± 0.2	14.8 ± 0.2	22.6 ± 0.4	58.7 ± 0.9
31	Humulene epoxide II	1610	65.3 ± 1.2	57.5 ± 0.8	33.6 ± 0.4	19.5 ± 0.4	63.0 ± 0.9	39.6 ± 0.7
32	Silphiperfol-6-en-5-one	1630	200.8 ± 2.9	89.8 ± 1.1	171.0 ± 1.6	400.1 ± 5.7	32.0 ± 0.8	40.7 ± 0.7
33	τ-Cadinol	1644	8.4 ± 0.6	38.5 ± 0.7	–	*	1.1 ± 0.1	16.8 ± 0.2
34	Epoxy-allo-alloaromadendrene	1645	–	–	*	6.9 ± 0.3	–	–
35	Khusinol	1680	–	237.4 ± 1.9	–	44.0 ± 0.6	–	–
36	Oplopanone	1750	*	24.9 ± 0.3	*	14.0 ± 0.2	*	15.0 ± 0.5
37	Methyl palmitate	1926	30.4 ± 0.9	60.7 ± 1.3	22.5 ± 0.4	31.5 ± 0.6	26.9 ± 0.5	27.1 ± 0.3
38	Methyl linoleate	2097	8.7 ± 0.4	7.7 ± 0.3	24.0 ± 0.4	11.2 ± 0.2	12.3 ± 0.2	7.6 ± 0.1
39	β-Amyrine	n.d.	152.1 ± 6.0	180.1 ± 5.0	152.1 ± 6.1	192.1 ± 6.3	104.1 ± 5.6	236.1 ± 5.7
40	α-Amyrine	n.d.	112.1 ± 4.5	144.1 ± 3.0	40.0 ± 0.8	60.0 ± 1.2	112.1 ± 5.4	160.1 ± 4.5

*Below detection limit – 0.1 μg/ml.

Studies revealed that fatty acids sum contents in initial (sample "0") sunflower oil was about 70% of fat with dominating PUFA (linoleic acid–about 41%), MUFA (oleic acid–about 19%), and SFA (about 9%) (Figs. 1–6, Table 7).

The experiment was also aimed at proving the influence of temperature (90 °C) and storage under experimental conditions on fatty acids concentrations in studied sunflower oil – a decrease of fatty acids contents was observed (Figs. 1–6, Table 7). Concentrations of fatty acids in studied oil decreased due to heating – after 120 h, that drop amounted to about 5% in relation to initial sample. Decrease of fatty acids sum by about 4% was recorded in sunflower oil samples stored at room temperature for 180 days. Comparison

Table 4
Concentrations of particular components in hexane (HEX) and ethanol (ET) extracts made of *Silphium* inflorescences

No.	Compound	Retention index	Concentration (g/ml)					
			S. perfoliatum		*S. trifoliatum*		*S. integrifolium*	
			HEX	ET	HEX	ET	HEX	ET
1	α-Pinene	938	44.0 ± 0.4	32.0 ± 0.5	20.0 ± 0.5	16.0 ± 0.4	16.0 ± 0.3	16.0 ± 0.2
2	Camphene	949	12.8 ± 0.1	*	5.5 ± 0.1	*	5.4 ± 0.1	0.5 ± 0.0
3	β-Pinene	975	*	*	*	*	*	*
4	Limonene	1031	*	5.1 ± 0.2	*	11.3 ± 0.3	8.9 ± 0.2	11.1 ± 0.1
5	Trans-verbenol	1148	15.2 ± 0.1	67.0 ± 0.8	16.0 ± 0.4	103.3 ± 2.5	2.6 ± 0.1	46.8 ± 0.6
6	Verbenone	1217	21.5 ± 0.2	10.7 ± 0.2	*	*	6.2 ± 0.1	0.5 ± 0.0
7	Bornyl acetate	1286	–	–	–	–	20.4 ± 0.3	31.2 ± 0.4
8	α-Copaene	1375	*	*	15.7 ± 0.3	0.4 ± 0.0	*	*
9	(E)-Caryophyllene	1420	17.2 ± 0.1	22.3 ± 0.4	61.4 ± 1.2	64.4 ± 0.8	11.3 ± 0.2	14.4 ± 0.2
10	α-Humulene	1455	*	*	32.7 ± 0.6	39.1 ± 0.5	1.5 ± 0.0	2.3 ± 0.1
11	Germacrene D	1480	23.8 ± 0.2	25.4 ± 0.4	24.2 ± 0.5	28.1 ± 0.4	27.6 ± 0.4	31.9 ± 0.4
12	Allo-aromadendr-9-ene	1490	–	–	–	–	35.5 ± 0.5	35.2 ± 0.4
13	γ-Cadinene	1515	–	–	5.2 ± 0.1	0.4 ± 0.0	*	*
14	(E)-Nerolidol	1560	–	–	–	–	–	–
15	Spathulenol	1578	36.9 ± 0.3	39.6 ± 0.6	29.9 ± 0.3	28.8 ± 0.4	1.5 ± 0.1	1.1 ± 0.1
16	Caryophyllene oxide	1582	49.3 ± 0.4	61.6 ± 0.8	193.3 ± 2.8	208.2 ± 3.0	50.5 ± 0.8	65.8 ± 1.0
17	Salvial-4(14)-en-1-one	1596	21.4 ± 0.2	27.7 ± 0.4	20.1 ± 0.4	30.8 ± 0.4	*	*
18	Humulene epoxide II	1610	15.5 ± 0.1	31.0 ± 0.6	69.6 ± 0.9	74.1 ± 0.9	26.8 ± 0.3	29.9 ± 0.4
19	Silphiperfol-6-en-5-one	1630	47.1 ± 0.4	129.7 ± 1.9	16.9 ± 0.3	120.4 ± 1.4	4.2 ± 0.1	4.6 ± 0.1
20	τ-Cadinol	1644	27.3 ± 0.3	50.4 ± 0.6	*	*	26.8 ± 0.4	41.6 ± 0.5
21	Epoxy-allo-alloaromadendrene	1645	42.0 ± 0.4	73.6 ± 0.9	10.3 ± 0.3	19.5 ± 0.2	–	–
22	Khusinol	1680	–	72.3 ± 1.1	–	43.5 ± 0.4	–	–
23	Oplopanone	1750	12.5 ± 0.2	21.5 ± 0.3	11.6 ± 0.2	18.0 ± 0.1	2.6 ± 0.1	8.2 ± 0.2
24	Methyl palmitate	1926	26.5 ± 0.2	58.9 ± 0.7	57.0 ± 0.9	64.2 ± 0.6	138.7 ± 1.3	189.0 ± 1.6
25	Methyl linoleate	2097	44.1 ± 0.4	36.2 ± 0.4	61.0 ± 1.0	37.3 ± 0.5	122.3 ± 1.1	84.3 ± 0.8
26	β-Amyrine	n.d.	96.0 ± 4.4	152.1 ± 4.0	160.1 ± 8.4	168.1 ± 8.0	100.1 ± 2.3	168.1 ± 8.3
27	α-Amyrine	n.d.	720.4 ± 35.2	940.5 ± 30.0	416.2 ± 17.4	420.2 ± 5.3	232.1 ± 3.2	324.2 ± 6.9

*Below detection limit – 0.1 μg/ml.

Table 5
Concentrations of particular components in hexane (HEX) and ethanol (ET) extracts made of *Silphium* rhizomes

No.	Compound	Retention index	Concentration (g/ml)					
			S. perfoliatum		*S. trifoliatum*		*S. integrifolium*	
			HEX	ET	HEX	ET	HEX	ET
1	α-Pinene	938	*	*	*	*	*	*
2	Camphene	949	1.6 ± 0.1	*	–	–	–	–
3	7-α-H-Silphiperfol-5-ene	1324	48.0 ± 0.6	52.0 ± 0.6	68.0 ± 0.6	88.0 ± 0.9	3.0 ± 0.1	2.9 ± 0.1
4	δ-Elemene	1335	7.1 ± 0.1	7.7 ± 0.2	5.0 ± 0.1	6.8 ± 0.1	4.3 ± 0.1	5.9 ± 0.2
5	7-β-H-silphiperfol-5-ene	1343	33.2 ± 0.4	35.6 ± 0.4	61.6 ± 0.6	80.0 ± 0.8	25.7 ± 0.4	26.7 ± 0.3
6	Aristolene	1346	16.0 ± 0.1	17.6 ± 0.2	11.1 ± 0.1	13.9 ± 0.1	8.0 ± 0.2	9.6 ± 0.2
7	α-Longipinene	1350	13.2 ± 0.1	12.7 ± 0.1	–	–	–	–
8	Silphiperfola-5,7(14)-diene	1357	4.1 ± 0.1	7.9 ± 0.1	2.9 ± 0.1	7.2 ± 0.1	–	–
9	Silphiperfol-6-ene	1373	2.5 ± 0.0	2.6 ± 0.1	5.1 ± 0.1	5.7 ± 0.1	*	*
10	α-Copaene	1375	3.5 ± 0.1	*	*	*	–	–
11	β-Maaliene	1382	25.4 ± 0.2	31.5 ± 0.3	4.7 ± 0.1	6.2 ± 0.1	30.9 ± 0.5	33.7 ± 0.3
12	α-Isocomene	1389	32.0 ± 0.4	42.2 ± 0.5	4.7 ± 0.1	5.1 ± 0.1	36.0 ± 0.4	37.0 ± 0.4
13	β-Isocomene	1412	10.7 ± 0.1	12.2 ± 0.2	4.5 ± 0.1	4.4 ± 0.1	6.2 ± 0.1	15.8 ± 0.2
14	(E)-Caryophyllene	1420	6.1 ± 0.1	8.4 ± 0.2	6.6 ± 0.1	9.1 ± 0.1	5.3 ± 0.1	7.4 ± 0.1
15	α-Humulene	1456	6.6 ± 0.1	10.2 ± 0.2	12.2 ± 0.1	37.9 ± 0.4	3.2 ± 0.1	4.7 ± 0.1
16	Germacrene D	1482	3.3 ± 0.1	8.7 ± 0.2	1.7 ± 0.0	2.8 ± 0.1	2.4 ± 0.1	3.2 ± 0.1
17	Allo-aromadendr-9-ene	1490	–	–	–	–	3.2 ± 0.1	1.6 ± 0.1
18	Drim-8(12)-ene	1496	4.8 ± 0.1	1.3 ± 0.0	–	–	3.4 ± 0.1	1.1 ± 0.0
19	Cubebol	1517	2.9 ± 0.1	1.3 ± 0.1	2.3 ± 0.1	1.0 ± 0.1	–	–
20	Caryophyllene oxide	1584	12.1 ± 0.1	17.1 ± 0.2	6.1 ± 0.1	9.1 ± 0.2	8.7 ± 0.1	8.1 ± 0.2
21	Presilphiperfolan-8-ol	1590	6.9 ± 0.1	13.0 ± 0.1	–	–	4.8 ± 0.1	5.2 ± 0.1
22	Humulene epoxide II	1610	8.5 ± 0.1	12.9 ± 0.1	8.0 ± 0.1	11.2 ± 0.2	34.0 ± 0.3	39.8 ± 0.3
23	Silphiperfol-6-en-5-one	1630	60.9 ± 0.9	195.7 ± 1.8	29.7 ± 0.3	80.6 ± 1.0	33.3 ± 0.4	64.0 ± 0.6
24	(E)-Coniferyl alcohol	1742	–	23.8 ± 0.3	–	13.9 ± 0.2	–	8.6 ± 0.2
25	Ambroxide	1763	*	*	*	*	2.8 ± 0.1	*
26	16-acetoxycarterochaetol	2787	62.1 ± 1.0	310.1 ± 2.6	66.9 ± 0.7	264.4 ± 2.9	93.0 ± 1.1	383.1 ± 3.2
27	β-Amyrine	n.d.	48.0 ± 0.3	52.0 ± 1.0	32.0 ± 0.6	144.1 ± 3.3	56.0 ± 0.6	64.0 ± 1.2
28	α-Amyrine	n.d.	164.1 ± 1.5	172.1 ± 3.8	28.0 ± 0.5	44.0 ± 0.9	52.0 ± 1.1	56.0 ± 0.9

*Below detection limit – 0.1 μg/ml.

of studies upon control with BHA-treated samples revealed that application of a synthetic anti-oxidant caused a protection effect towards fatty acids contained in samples – their contents remained at comparable levels to the initial sample "0".

Table 6
Content of fatty acids sum in *Silphium* ethanol and hexane extracts

Species	Organs	Fatty acids contents (g/ml)	
		Ethanolic extracts	Hexane extracts
S. prefoliatum	Leaves	*	*
	Inflorescences	*	*
	Rhizomes	*	*
S. trifoliatum	Leaves	*	*
	Inflorescences	*	*
	Rhizomes	*	*
S. integrifolium	Leaves	*	*
	Inflorescences	*	*
	Rhizomes	*	*

*Below detection limit – 0.10 mg/ml.

Figs. 1–8 illustrate the influence of *Silphium* extracts addition on changes of fatty acids contents in heated and stored sunflower oil. Maximum decrease of PUFA and MUFA (about 5% each) was observed in heated control samples and those from *S. perfoliatum* rhizome extracts (Fig. 1). After 120 h of heating, oil with *Silphium* rhizome extract addition was characterized by higher (from 2% to 5%) content of linoleic acid in relation to control sample with no extract addition. A great similarity in the impact of *Silphium* extracts and BHA on quantitative composition of fatty acids in sunflower oil stored under experimental conditions (180 days) and heated (for 120 h) could be observed.

Values of linoleic acid change inhibition in samples stored at room temperature were at positive levels (change inhibition) within the range of 0.01% (hexane extract made of *S. perfoliatum* leaves,

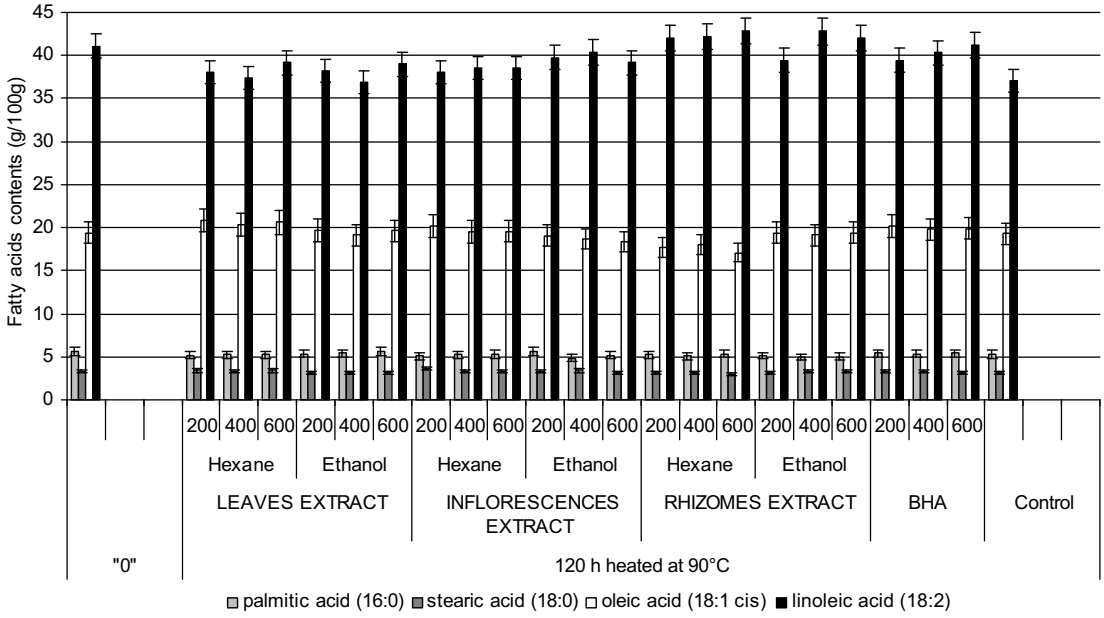

Fig. 1. Content of fatty acids in sunflower oil with addition of extracts made of *S. perfoliatum* heated at 90 °C for 120 h designations as in Table 1.

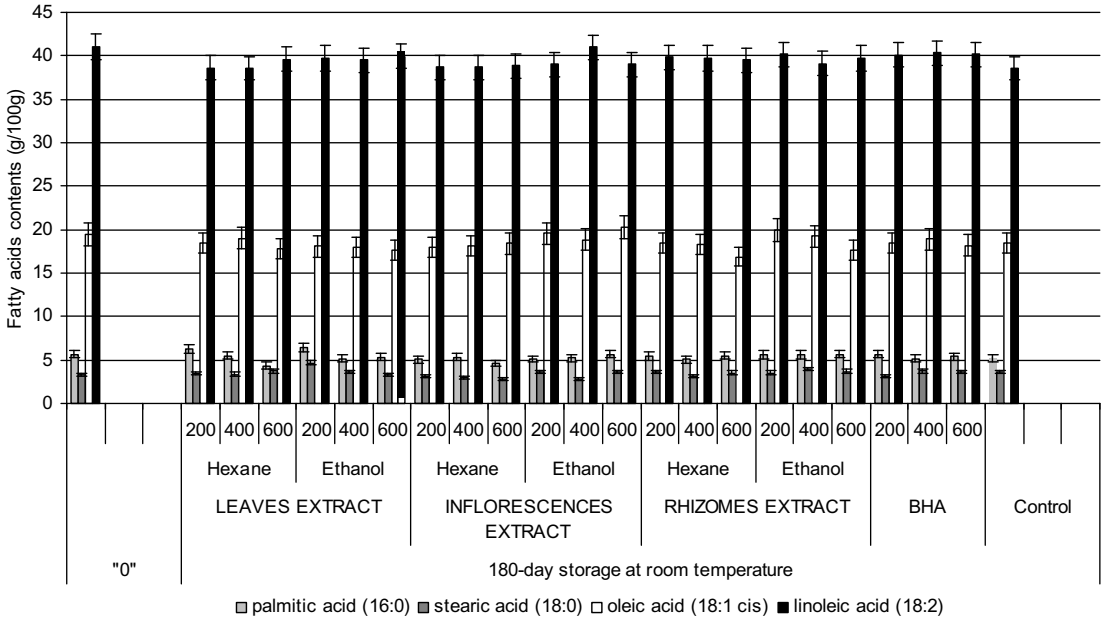

Fig. 2. Content of fatty acids in sunflower oil, with addition of extracts made of *S. perfoliatum*, stored at room temperature for 180 days designations as in Table 1.

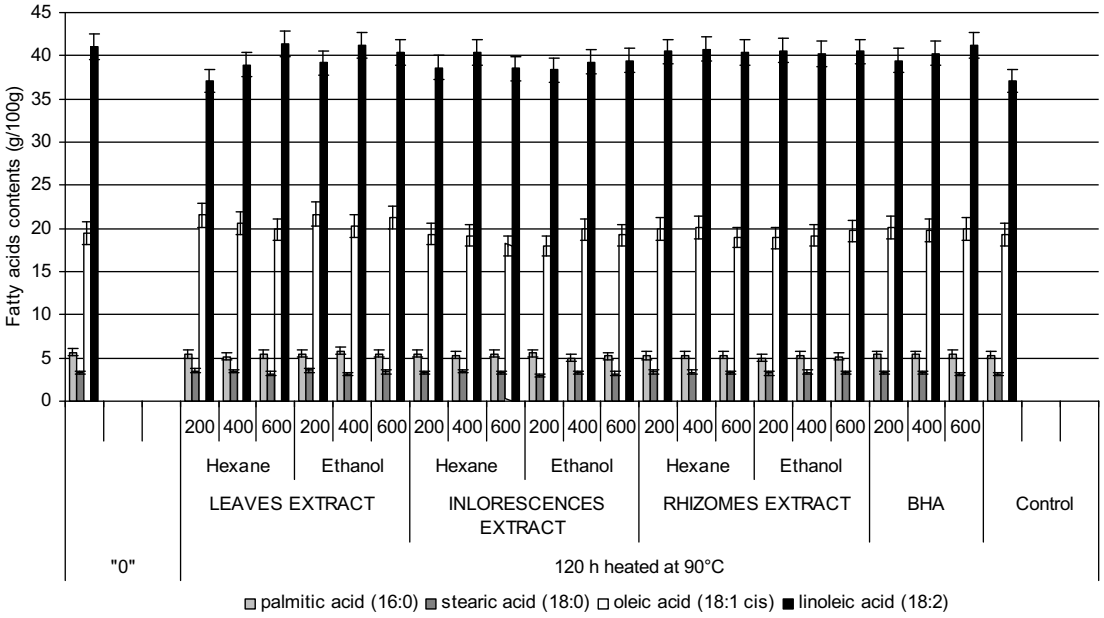

Fig. 3. Content of fatty acids in sunflower oil with addition of extracts made of *S. trifoliatum* heated at 90 °C for 120 h designations as in Table 1.

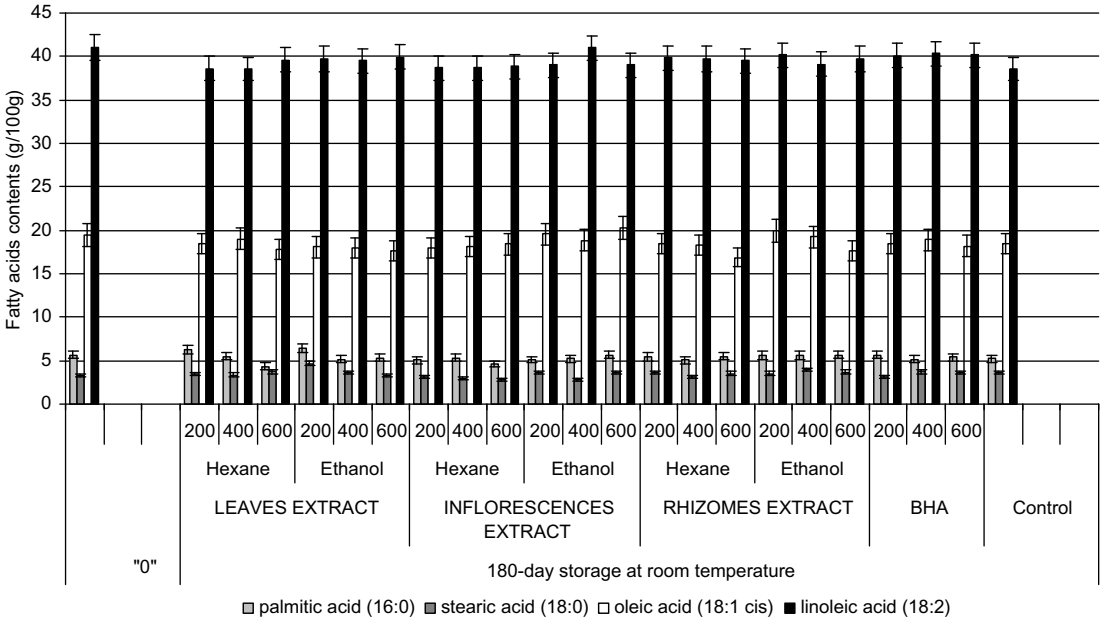

Fig. 4. Content of fatty acids in sunflower oil, with addition of extracts made of *S. trifoliatum*, stored at room temperature for 180 days designations as in Table 1.

400 μl) to 7.09% (hexane extract made of *S. trifoliatum* inflorescences, 400 μl); while negative values (change catalysis) were recorded only in two cases: $I_{h18:2} = -2.39\%$ (hexane extract made of *S. integrifolium* inflorescences, 600 μl) and $I_{h18:2} = -0.98\%$ (ethanolic extract made of *S. integrifolium* leaves, 200 μl). Values of change inhibition for linoleic acid in oil systems containing BHA and stored at ambient temperatures were: 4.04% for 0.02% BHA, 4.57% for 0.04% BHA, and 4.08% for 0.06% BHA.

In samples heated for 120 h with extracts addition, in general, positive influence of extracts and BHA on fatty acids contents was observed – value of inhibition was greater than zero (except for the system with ethanol extracts made of *S. perfoliatum* leaves – 400 μl at $I_{h18:2} = -0.56\%$). Hexane (600 μl) and ethanol (400 μl) extracts made of *S. perfoliatum* rhizomes were characterized by the highest change inhibition in relation to linoleic acid (Fig. 7): 15.69% and 15.53%, respectively. Systems with addition of *Silphium* leaves and inflorescences were distinguished by the highest change inhibition in reference to linoleic acid: 11.80% for sunflower oil with *S. trifoliatum* leaves extract and 8.99% (600 μl, hexane) with *S. trifoliatum* inflorescences extract (400 μl, hexane). When comparing the values of change inhibition for linoleic acid in oil systems containing BHA: $I_{h18:2} = 6.42\%$ for 0.02% BHA, or for 0.06% BHA – $I_{h18:2} = 11.32\%$, it can be found that *Silphium* extracts were not worse than BHA, and in some cases they were characterized by even higher change inhibition values.

In the case of BHA, it was proven that values of change inhibition for linoleic acid increased along with increase of the agent. However, the influence between the amount of *Silphium* extracts

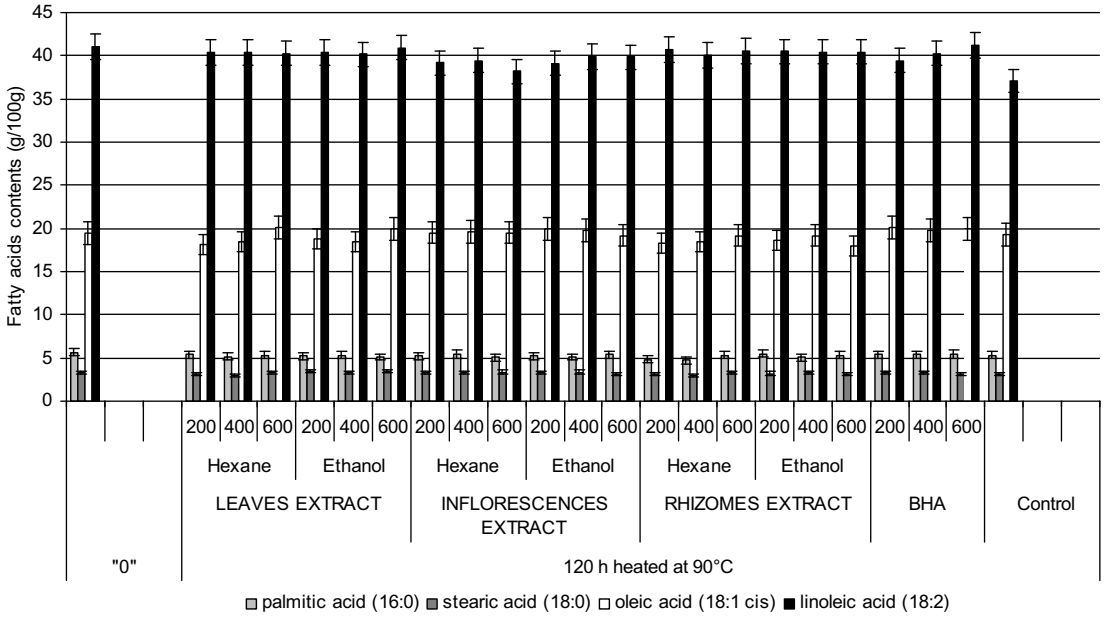

Fig. 5. Content of fatty acids in sunflower oil with addition of extracts made of *S. integrifolium* heated at 90 °C for 120 h designations as in Table 1.

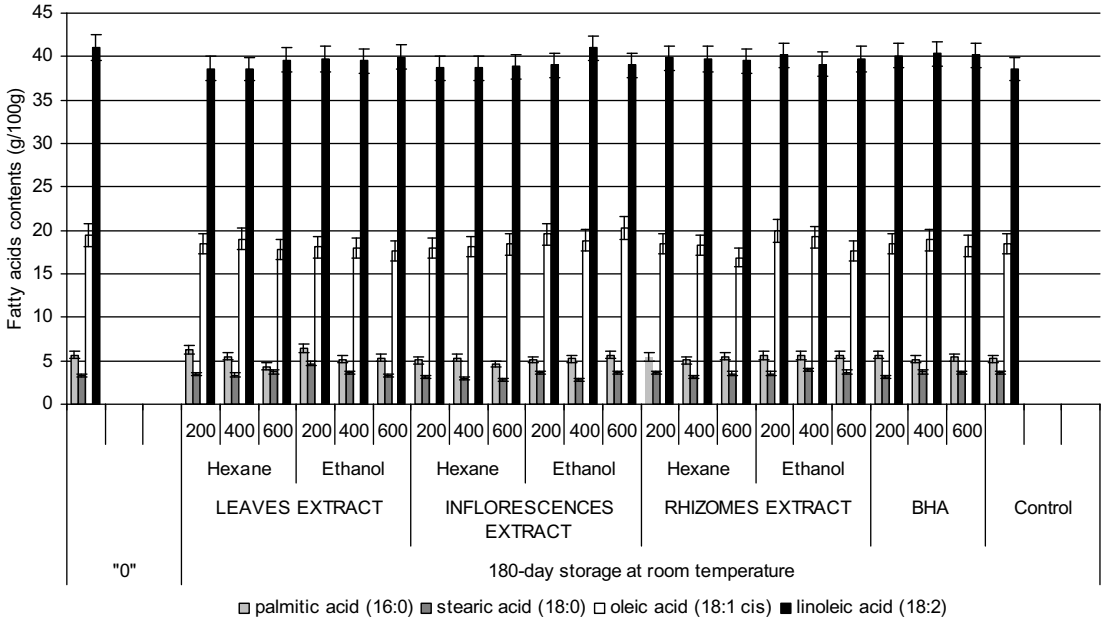

Fig. 6. Content of fatty acids in sunflower oil, with addition of extracts made of *S. integrifolium*, stored at room temperature for 180 days designations as in Table 1.

Table 7
Changes of fatty acids (FA) contents in sunflower oil during heating and storage

FA	Fatty acids contents					
	0		120		180rt	
	g/100 g of total lipids	Relative content %	g/100 g	Relative content %	g/100 g	Relative content %
PUFA	41.10 ± 0.83	59.13 ± 1.19	37.04 ± 1.25	57.20 ± 1.93	38.58 ± 0.95	58.61 ± 1.44
MUFA	19.44 ± 0.90	27.97 ± 1.29	19.30 ± 0.22	29.80 ± 0.34	18.42 ± 0.64	27.98 ± 0.97
SFA	8.97 ± 0.73	12.90 ± 1.05	8.42 ± 0.20	13.00 ± 0.31	8.83 ± 0.76	13.41 ± 1.15
SUM	69.50	100.00	64.75	100.00	65.83	100.00

0 – initial sample; 120 – 120-hour heating at 90 °C; 180rt – 180-day storage at room temperature.

added to the oil and inhibition value in tested system could not be univocally determined. Chemical diversity of added extracts caused that particular components might have synergistic interactions "within the extract" as well as active substances naturally

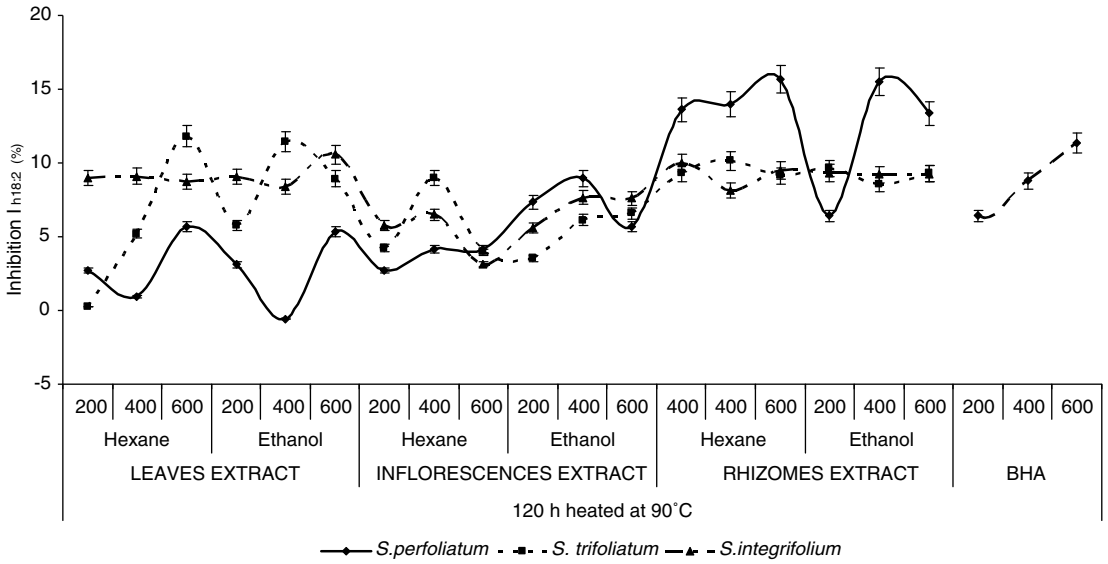

Fig. 7. Activity of *S. perfoliatum, S. trifoliatum, S. integrifolium* extracts determined as a quantitative changes of linoleic acid in sunflower oil heated at 90 °C for 120 h designations as in Table 1.

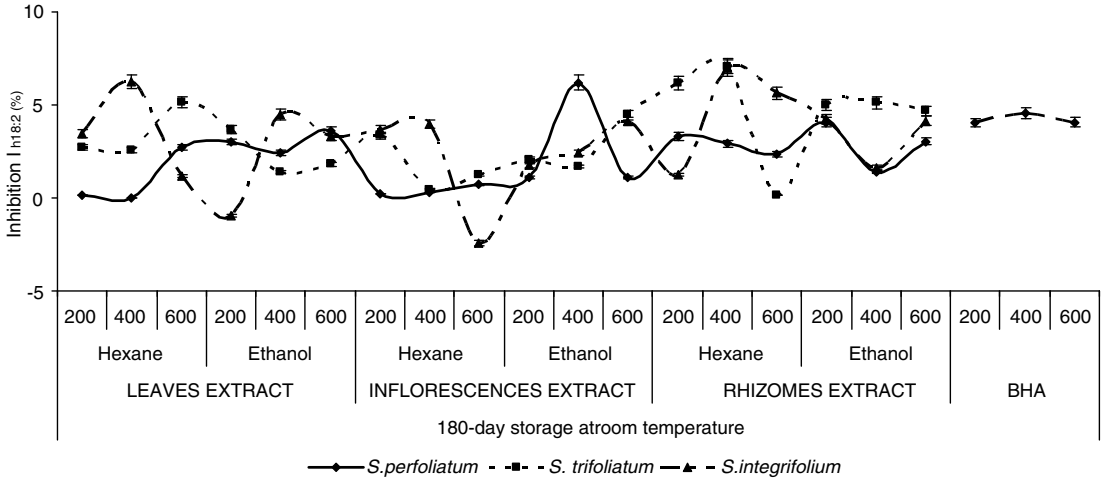

Fig. 8. Activity of *S. perfoliatum, S. trifoliatum, S. integrifolium* extracts determined as a quantitative changes of linoleic acid in sunflower oil stored at room temperature for 180 days designations as in Table 1.

occurring in studied oil and thus they might be inhibitors of quantitative change reaction (e.g. due to inhibition of oxidation, cyclization, or polymerisation), and catalysts (e.g. positively catalysing the oxidation, cyclization, or polymerisation processes) (Kowalski, 2007c).

In the present experiment, sunflower oil enrichment using extracts containing glycoside forms of oleanolic and ursolic acids was performed, and inhibition of changes in fatty acids composition was observed in many systems, which was the impulse to improve the oil properties. It can be supposed that glycosides of triterpene acids that inhibit unfavourable changes in fats may be one of significant components of extracts. The literature data indicate that these compounds are characterized by strong anti-oxidation properties (Assimopoulou, Zlatanos, & Papageorgiou, 2005; Chołuj & Janiszewska, 2005; Herrera, Rodriguez-Rodriguez, & Ruiz-Gutierrez, 2006; Kalogeropoulos, Ciou, Mylona, Ioannou, & Andrikopoulos, 2007; Perona, Arcemis, Ruiz-Gutierrez, & Catala, 2005), and therefore they may inhibit processes leading to structure conversions of fatty acids contained in a fat. Studies upon well-known and appreciated olive oil (Guinda, Pérez-Camino, & LanzÓn, 2004) revealed that its fat contains "natural" considerable amounts of those triterpene acids. Content of triterpene acids in olive oil is significant, thus technologies for enriching the fat in oleanolic acid have been developed (EP 1013752A1, 2000).

It is well-known that natural polyphenols occurring in oil plants stabilise oils produced by them, e.g. olive oil is very stable due to these substances presence (De Leonardis, Macciola, & Di Rocco, 2003; Sharma, Sharma, & Lal Kaushal, 2006). Unfortunately to date, pure, natural polyphenolic anti-oxidants did not find any wide application as opposed to artificial ones, despite their being safer in general. This is associated with difficulties during extraction and their low yield in pure form from plant materials. Furthermore, those substances may invoke discolorations, namely in the presence of heavy metals contained in products or packagings. Their other defects are: high costs for purification and insufficient solubility in fats (Oszmiański, 1995). Marinova and Yanishlieva (1996) found anti-oxidation activity of p-coumaric, ferulic, and caffeic acids in experimental systems for olive oil. They observed strong influence of the unsaturation type and degree of the lipid system on the kinetics and mechanism of the antioxidative action of the

phenolic acids. Kowalski (2007c) also studied the influence of quercetine, caffeic acid, and protocatechuic acid additives on quantitative changes of fatty acids in sunflower oil and olive oil, which led to conclusions about inhibition properties of these substances in tested systems. Other authors found inhibition effects of caffeic and chlorogenic acids on oxidation changes in heated sunflower oil (De Leonardis, Macciola, & Di Rocco, 2003). Addition of raw plant extracts is one of the latest solutions, the costs of which are lower and such mixtures of natural substances can be easier soluble in lipids (Abdalla & Roozen, 1999; Kovatcheva et al., 2001; Exarchou et al., 2002; Oberdieck, 2004; Pizzale, Bortolomeazzi, Vichi, Überegger, & Conte, 2002). In addition, toxicologic studies should be carried out before a given natural agent or extract is introduced into common utilization, because its natural origin itself does not guarantee it to be completely safe.

No doubt, the complex of compounds present in extracts from studied *Silphium* varieties affects their potential utility value, which was confirmed by earlier works on biological activity (Kujanceva & Davidjanc, 1988; Syrov et al., 1992; Davidjanc et al., 1997; Kowalski & Kędzia, 2007). Present paper confirms the activity of extracts made of *Silphium* varieties in inhibition of durable changes occurring in the structure of fatty acid triacylglycerols contained in stored and heated sunflower oil.

4. Conclusions

A positive effect of extracts made of *S. perfoliatum, S. trifoliatum*, and *S. integrifolium* leaves, inflorescences, and rhizomes added to the sunflower oil on durable quantitative composition of fatty acid profile was proven. Tested extracts elevated the value of change inhibition in reference of linoleic acid to a level comparable with BHA and sometimes, in appropriate systems, they were characterized by more advantageous value.

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