

## Potential Application of Oilseeds as Sources of Antioxidants for Food Lipids – a Review

ŠTEFAN SCHMIDT<sup>1</sup> and JAN POKORNÝ<sup>2</sup>

<sup>1</sup>*Faculty of Chemical and Food Technology, Slovak Technical University, Bratislava, Slovak Republic;* <sup>2</sup>*Department of Food Chemistry and Analysis, Faculty of Food and Biochemical Technology, Institute of Chemical Technology Prague, Prague, Czech Republic*

### Abstract

SCHMIDT Š., POKORNÝ J. (2005): **Potential application of oilseeds as sources of antioxidants for food lipids – a review.** Czech J. Food Sci., **23**: 93–102.

Oilseeds and other sources of edible oils contain both less polar antioxidants soluble in the oil phase, and more polar antioxidants, better soluble in the aqueous phase. Oilseeds which are consumed directly as such or after roasting may be added to foods in order to increase their stability against oxidation. The liposoluble antioxidants are extracted in crude oil during oilseed processing, and they are partially recovered in deodorisation sludges. More polar antioxidants remain in expeller cakes or extracted meal, which may be also used as food additives to increase the oxidative stability of foods. Oilseed meal extracted with hydrocarbons may be subsequently extracted with more polar organic solvents to obtain concentrates of phenolic substances, mainly phenolic acids, lignans or flavonoids. These are more active antioxidants, but also more expensive. Pure isolated antioxidants from oilseeds should be tested for their safety. In comparison with synthetic antioxidants, natural antioxidants from oilseeds have several advantages, but also disadvantages. The application should be considered from several aspects, such as antioxidant activity, safety, availability, effect on sensory value, and price.

**Keywords:** antioxidants; application in foods; edible oils; extracted oilseed meals; oilseeds; oxidation

The consumption of polyunsaturated vegetable oils has substantially increased since the World War II. The consequence of this change is a higher rate of the oxidation of the lipid fraction both in foods (KAMAL-ELDIN 2003) and *in vivo* (GUARDIOLA *et al.* 2002). Free radicals formed in these processes cannot be sufficiently regulated by natural mechanisms (PACKER 1996). A high concentration of free radicals can result in the initiation and development of different chronic diseases, such as cancer or atherosclerosis. Therefore, the need of efficient inhibition of the oxidation processes has become necessary (PACKER & ONG 1998). The easiest way is the application of anti-

oxidants directly to foods consumed in the diet. Preferentially, natural phenolic antioxidants are added to the food products, mainly ingredients of plant origin, generally consumed in the diet. The only difference should be higher levels of antioxidants in foods enriched with antioxidants than in common foods.

Efficient phenolic substances with antioxidant activity are found in vegetables, fruit, spices and cereals (SHAHIDI & NACZK 1995). Oilseeds also contain antioxidants which attracted, however, less attention for technical reasons than the antioxidants from the previously mentioned sources. The main reason is that oilseeds are less often directly

consumed, excepting, perhaps, nuts. We would like to review the potential use of oilseeds and oilseed products as sources of antioxidants.

### Fractionation of the oilseed antioxidants in course of oilseed processing

Oilseeds are rarely consumed directly, soybeans and peanut being exceptions. Walnuts, poppyseed and hazelnuts, which are rich in oils, are consumed, too, but they are used only as food ingredients or flavourings, and are not processed for the large scale production of edible oils. Soybean or peanut grits, flours, or pastes may be added to foods to improve their stability against oxidation. The disadvantage of this application is a substantial increase of the oil content and of the available energy in the resulting product.

Oilseeds are generally processed in the food industry to obtain edible oils (FILS 2000). Oilseeds are crushed and heated to inactivate enzymes, and to destroy the bonds between lipid and protein moieties in membranes and lipoproteins. In the production of virgin (cold-pressed) oils, this processing step is omitted. Oil is then partially removed from the heated meal by expeller pressing under high pressure and at temperatures up to 100°C. In materials with low oil content, the pressing may be omitted. Crude oil is filtered and collected.

The remaining oilseed cakes usually contain 5–20% oil, and are further processed by solvent extraction, most often with hexane or mixtures of hydrocarbons. Exceptionally, they may be extracted with liquid carbon dioxide. Miscella containing oil dissolved in the solvent is then removed, and the solvent is distilled off. Crude oil obtained in this way is usually combined with crude oil obtained by expeller pressing. The remaining extracted meals are purified from residual solvents. In the production of virgin (cold-pressed) oils, the second stage of solvent extraction is omitted.

During the processing, natural antioxidants present in original oilseeds are fractionated into the liposoluble and hydrophilic fractions. Most lipophilic antioxidants are extracted into crude oil during the expeller pressing and solvent extraction. Some antioxidants of medium polarity are also partially extracted. More polar natural antioxidants in crude oils are partially removed during the oil refining. Antioxidants remaining in the extracted meal are not significantly damaged during the oilseed processing.

### Antioxidants in crude and refined vegetable oils

The natural antioxidants present in vegetable oils belong to two groups of compounds. Tocopherols, carotenoid pigments and some sterols are found in all crude oils. Other antioxidants, derived from lignans, are present only in the minority of oils. The most important group of natural antioxidants present in crude and refined edible oils are tocopherols (KAMAL-ELDIN & APPELQVIST 1996). The most active antioxidant *in vivo* among them is  $\alpha$ -tocopherol. On the contrary, the most active antioxidants in bulk food lipids are  $\gamma$ -tocopherol and  $\delta$ -tocopherol, but the last compound is usually present only in very small amounts. The tocopherol content in the most important oils and oil fractions of oilseeds is shown in Table 1. The closely related tocotrienols, present in palm oil and oil from cereals, possess antioxidant activities similar to that of tocopherols. Tocopherols are partially removed from crude oil during its deodorisation, but the final amount is still sufficient to protect refined oils against oxidation. Tocopherols are present in vegetable oils in concentrations nearly corresponding to the optimum activity (HEIMANN & VON PEZOLD 1957). The oxidative stability of oils cannot be increased efficiently by the addition of pure tocopherols or of other oils containing only tocopherols as natural antioxidants. An exception is the addition of oils rich in  $\gamma$ -tocopherol to oils containing  $\alpha$ -tocopherol as the major antioxidant and only traces of  $\gamma$ -tocopherol. Oils containing only tocopherols, especially corn oil, can increase the stability of animal fats containing no natural antioxidants.

Carotenoid pigments present in crude oils also have antioxidant activity, especially in the light, but also *in vivo* (PALOZZA & KRINSKY 1992). They are, however, almost completely removed in the course of oil refining (OOI *et al.* 1996; FAESSELT 1998). Of course, they may be added back to the refined oil, at least in the case of palm oil. Some sterols, e.g. avenasterols (9), present in some oils, contribute to the resistance against oxidation (BOSKOU & MORTON 1976; BOSKOU 1996).

Some oils contain other antioxidants, too, mainly from the group of lignans. Lignans are compounds containing bound phenolic acids. Most of them are insoluble during oilseed processing, but a small fraction of lignans is decomposed. The decomposition products are partially dissolved in crude oil. Only a few examples will be given here, which are important

Table 1. Tocopherol contents (mg/kg oil) in some vegetable oils (FIRESTONE 1996)

Vegetable oil	$\alpha$ -Tocopherol	$\beta$ -Tocopherol	$\gamma$ -Tocopherol	$\delta$ -Tocopherol
Soybean oil	9–352	0–36	89–2307	154–932
Sunflower oil	403–935	< 45	0–34	0–7
Rapeseed oil	100–386	< 140	189–753	0–22
Peanut oil	49–373	< 41	88–389	50
Sesame oil	0–3	0	521–983	4–21
Safflower oil	234–660	0–17	0–12	0
Corn oil	23–573	< 356	268–2468	23–75
Olive oil	90	–	10	–
Walnut oil	10–20	–	263–400	46–60
Coconut oil	0–17	< 11	0–14	0
Cacao butter	1–19	< 10	18–196	0–17

in oil technology. Sesamol and related compounds are present in sesame oil, contributing to the excellent resistance of sesame oil against rancidification. Oryzanol in rice bran oil originates from rice bran antioxidants. Oryzanol is no single compound, but a group of esters of phenolic acids, mainly ferulic acid, with sterols. Because of the bound sterols, the polarity of oryzanol is relatively low. Rice bran antioxidants are mainly concentrated in unsaponifiables (GOPALA KRISHNA *et al.* 2003).

A group of derivatives of hydroxytyrosol is present in olive oil. These are formed by decomposition of more polar precursors, which remain in the residue (pomace) after the removal of oil. Their antioxidant activity will be treated in the discussion on the activity of oilseed cakes or extracted meals, as a substantial part remains there even after the extraction of crude oil. Their content decreases during ripening of olives (CINQUANTA *et al.* 2001) so that the olive fruits used for oil production are less rich in antioxidants than green olives. An addition of these oils rich in antioxidants other than tocopherols can increase the resistance against oxidation both under storage and frying conditions (GUPTA *et al.* 2004). An example is GoodFry oil which is a mixture of high-oleic sunflower oil with sesame and rice bran oils (BERGER 1998). The product is a stable frying oil.

#### Antioxidants present in extracted oilseed meals

Extracted oilseed meals contain only negligible residues of liposoluble antioxidants. More polar

antioxidants, present in extracted meals, consist of phenolic acids, either free or esterified or condensed in insoluble compounds. Another important antioxidant fraction is flavonoids, which can be detected in nearly all extracted meals, at least in small amounts. The minority of extracted meals contain lignans and their decomposition products. A great amount of published experimental evidence exists on the subject so that only a short summary and a few typical examples will be given here.

Extracted meals containing only phenolic acids and flavonoids will be discussed in the first place. Some substances possessing antioxidant activities have been detected in most expeller cakes and extracted meals, such as phenolic acids, e.g. caffeic, dihydrocaffeic acids (NENADIS *et al.* 2003), ferulic and sinapic acids, or flavonoids. Many phenolic substances are common in several oilseeds, as shown in Table 2. Rapeseed meal is very rich in phenolics (77–81 mg/kg), mainly sinapic acid (AMAROWICZ *et al.* 2001). However, sinapic acid is bound to choline forming sinapine, which is almost inactive as an antioxidant (KRYGIER *et al.* 1982; XU & DIOSADY 1997). Mustard seed contains similar antioxidants as rapeseed.

Soybean flour or defatted flour has been used as an antioxidant since the beginning of food stabilisation (MUSHER 1936) but the antioxidant activity was intensively studied even later, because of the presence of isoflavones and cinnamic acid derivatives (ARAI *et al.* 1966). The antioxidant activity of aqueous extracts is attributed to genistein and glycitein 7-O-monoglucosides (PRATT & BIRAC 1979). The antioxidant activity of soybean hy-

Table 2. Antioxidants identified in oilseed extracted meals of cakes

Oilseed	Substances with antioxidant activities	References
Rapeseed, canola	sinapine, benzoic and cinnamic acid derivatives, phenolic acid esters and glycosides	a, b, c, d
Mustard seed	sinapine, esters of phenolic acids	a e, f, h
Soy beans	syringic, vanillic, ferulic, salicylic, <i>p</i> -coumaric acids and esters, chlorogenic, caffeic, sinapic acids, isoflavones and their glucosides	k, e, l, m, n
Peanuts	phenolic acids and esters, such as <i>p</i> -hydroxybenzoic, <i>p</i> -coumaric, syringic, ferulic, caffeic acids	f
Sunflower seed	chlorogenic, caffeic, <i>p</i> -hydroxybenzoic, <i>p</i> -coumaric, cinnamic, <i>m</i> -hydroxybenzoic, vanillic, syringic, gallic, and vanillic acids, epicatechin, catechin	o, p
Evening primrose seed	proanthocyanidines and their gallates, isoflavones	s, t, u, v, w
Linseed	sinapic, <i>p</i> -hydroxybenzoic, coumaric, ferulic acids, lignans and their glucosides	e, f, x, y, z
Cottonseed	sinapic, ferulic, <i>p</i> -hydroxybenzoic acids, quercetin, rutin	e, f, A
Sesame seed	lignans, coumaric, ferulic, vanillic, sinapic acids	C, e, f
Olive fruits, cakes	hydroxytyrosol, secoiridoids, flavonoids, lignans	D, E
Grapeseed	catechin, epicatechin, procyanidin	F, G, H

## Explanation to symbols:

a – DABROWSKI & SOSULSKI (1984)	n – MURAKAMI <i>et al.</i> (1984)	z – JOHNSON <i>et al.</i> (2000)
b – KOZŁOWSKA <i>et al.</i> (1983)	o – LEUNG <i>et al.</i> (1981)	A – HRON <i>et al.</i> (1999)
c – KRYGIER <i>et al.</i> (1982)	p – SABIR <i>et al.</i> (1974)	C – FUKUDA <i>et al.</i> (1986a, b)
d – AMAROWICZ <i>et al.</i> (2000)	s – AMAROWICZ <i>et al.</i> (1999)	D – GUTFINGER (1981)
e – AMAROWICZ <i>et al.</i> (1996)	t – SHAHIDI <i>et al.</i> (1997)	E – GENNARO <i>et al.</i> (1998)
f – HENNING (1982)	u – ZADERNOWSKI <i>et al.</i> (1996)	F – FULEKI & DASILVA (1997)
h – KRYGIER <i>et al.</i> (1982)	v – NIKLOVÁ <i>et al.</i> (2001)	G – JAYAPRAKASHA <i>et al.</i> (2001)
k – WALTER (1941)	w – SCHMIDT <i>et al.</i> (1998)	H – TERESA <i>et al.</i> (1992)
l – ARAI <i>et al.</i> (1966)	x – AMAROWICZ & SHAHIDI (1994)	
m – HOPPE <i>et al.</i> (1997)	y – AMAROWICZ <i>et al.</i> (1994)	

drolysates is probably mostly due to isoflavone aglycones (MURAKAMI *et al.* 1984).

The antioxidant activity of peanuts is mainly due to phenolic acids (PRATT 1984). Defatted sunflower meal contained 3.0–3.5 g/kg phenolics; chlorogenic and caffeic acids constitute about 70% of phenolic antioxidants (SABIR *et al.* 1974).

The main antioxidant in defatted rice bran flour is  $\gamma$ -oryzanol, which is a mixture of sterol ferulates with related compounds (XU *et al.* 2001; GOPALA KRISHNA *et al.* 2003). Defatted grapeseed meal contains a mixture of catechins and procyanidins (SAITO *et al.* 1998).

Evening primrose seeds are used for the extraction of oil used for dietetic purposes. Extracted meal is rich in phenolics (ZADERNOWSKI *et al.* 1996), including proanthocyanidins, catechins, polymerised polyphenols, and isoflavones (SHAHIDI *et al.* 1997). Fractions obtained by extraction with ethyl

acetate were found active, especially those containing phenolic acids (SCHMIDT *et al.* 2003).

Extracted meals containing lignan derivatives originate from the same sources as mentioned in the discussion of oils. The main precursors of sesame seed antioxidants are lignans, such as sesamol (FUKUDA *et al.* 1986a, b). Methanolic extract of defatted sesame flour contained 41 mg/kg free phenolic acids, 325 mg/kg esterified acids and 14 mg/kg insoluble phenolic acids (KOZŁOWSKA *et al.* 1984). The antioxidant activity of lignan derivatives – sesamin, sesamol and sesamol – has been known since more than 50 years ago (BUDOWSKI 1950). Sesamol and other lignan decomposition products are more active than the original lignans (DACHTER *et al.* 2003). Similar lignans were found in linseed, contributing to the favourable dietetic effect of linseed consumption (RICKARD & THOMPSON 1997).

Olive fruit is rich in phenolic antioxidants, mostly extractable with methanol (NINFALI *et al.* 2001). They consist of simple phenols (hydroxytyrosol and tyrosol), secoiridoids, such as oleuropein and its aglycone, flavonoids, and lignans (TSIMIDOU *et al.* 1992; BRENES *et al.* 2000). Their contents change during the ripening (ROVELLINI & CORTESI 2003). The difficulty of olive cakes (pomace) are that they are unstable in storage because of a high water content. Therefore, they can be added to foods only exceptionally.

#### **Antioxidants present in oilseed shells and husks**

Oilseeds are often protected by husks or shells which are mainly removed before the oilseed processing as their oil content is low. Husks are used as feed or fuel, but they have relatively high contents of phenolics in some cases, usually higher than are their contents in seeds, so can be used as sources of antioxidants.

In husks and skins of oilseeds, the same substances are usually present as those in kernels, and different tannins and proanthocyanidins are also present. Several types of proanthocyanidins and flavonoids were identified in peanut skin (LOU *et al.* 2004). High molecular weight oleoresins found on the surfaces of oilseeds are co-extracted with phenolics and contribute significantly to the antioxidant activity of the extracts (MURPHY *et al.* 1993). Rapeseed hulls have a high content (between 2–6 %) of condensed tannins (AMAROWICZ *et al.* 2001; NACZK *et al.* 2000). Peanut hulls (skins) are a particularly rich source of phenolics, containing tannins, procyanidins, catechin and epicatechin oligomers, resveratrol, and other phenolic substances (KARCHESY & HEMMINGWAY 1986). Sunflower seed shells are rich in chlorogenic acids; caffeic acid can be isolated from the aqueous-ethanolic extract after saponification (DELEONARDIS *et al.* 2005). Hazelnut hulls contain high concentrations of phenolics (MOURE *et al.* 2003).

#### **Extraction of antioxidants from cakes and extracted meals**

The extracted meals are readily available, but they have no sufficiently high content of phenolics to be used directly as food ingredients. Therefore the applications of various extraction processes were proposed by many authors. The extracted meals

have been already extracted with hydrocarbon solvents. Further extraction with hexane or other hydrocarbon solvents is thus not efficient as tocopherols and other lipophilic antioxidants have been previously removed during the extraction of oil, and polar antioxidants have only low solubility in nonpolar solvents. Solvents of medium polarity, such as acetone or ethyl acetate, are more useful for the extraction of efficient antioxidants (POKORNÝ & KORCZAK 2001), but these solvents are relatively expensive. Aqueous ethanol or methanol (80–90%) are suitable for the extraction of polar antioxidants, such as flavonoids or phenolic acids. The antioxidants obtained with these solvents would be acceptable for fat dispersions, such as with meat products. Ethanol extracts of rapeseed meals were more efficient antioxidants in the concentration of 0.05–0.10% than BHA, BHT, and monoacylglycerol citrate added in 0.02% concentrations (WANASUNDARA & SHAHIDI 1994).

The extraction with supercritical carbon dioxide is excellent as the extract would be relatively pure, but the procedure is rather expensive.

#### **Differences between antioxidant activities in bulk fats and oils and in food dispersions**

The efficiency of antioxidants isolated from oilseeds depends very much on the conditions of their application in foods. The activities of antioxidants depend very much on their polarity. Lipophilic antioxidants are more active in emulsions while polar antioxidants are more active in bulk fats and oils (FRANKEL 1993). The concentration of free radicals and the rate of their formation, depending on the temperature and oxygen access, also play a role. Antioxidants from extracted oilseed meals will be hardly used for the stabilisation of bulk fats as they are not soluble in the oil phase. They will be probably used for the protection of food dispersions against oxidative deterioration. The antioxidant activity of olive fruit antioxidants was found different in oil and in oil-in-water emulsions (PAIVA-MARTINS & GORDON 2002). Food dispersions contain many substances, dissolved in the oil phase, soluble in the aqueous phase or nearly insoluble. Many food components affect the antioxidant activity in the positive or in the negative way so that the actual activity of antioxidants in real foods is difficult to predict, and should be determined by experiment.

### **Properties other than antioxidant activity to observe when applying oilseed antioxidants in foods**

Many natural materials are tested for their antioxidant activity and recommended for food applications, but the authors do not sufficiently take other aspects in consideration, such as the safety aspects, prospective availability, or price. Therefore, these aspects will be briefly discussed. It should be remembered that the importance of these aspects is very difficult to be determined quantitatively, as it depends on many factors which are rapidly changing.

### **Comments on food safety when applying oilseed antioxidants**

The standpoint of safety is now of primary importance in the food production. Nevertheless, the standpoint of safety of natural antioxidants as food additives is often neglected. Many scientists propose new natural antioxidants without caring about their effects on the human health. The occurrence of a compound in natural materials, even those used as foods, is no guarantee of their safety when applied at higher concentrations than it corresponds to the daily intake in food.

Several oilseeds are used as food, such as soybeans, sunflower seeds, peanuts, sesame seeds, olives, coconuts, and other nuts. There would be no objections from the safety standpoint against their application as such, or as cakes or extracted meal. The extracts obtained with organic solvents, especially purified substances, should be first proved for their safety by about the same tests as in the case of synthetic substances. Naturally, solvent residues should not be absent.

More problems can be expected in the case of oilseeds, used only for the production of oils or as feed. Consumers may object to their application as food ingredients as they are not used to them as food components. The same regulations should be valid for the use of extracts as for non-food materials, and the concentrations proposed as food additions should be tested for safety.

As the preparations of antioxidants from oilseeds are less concentrated than synthetic antioxidants, they are less efficient than synthetic antioxidants. Therefore, larger additions of oilseed antioxidants are necessary, which should be considered when evaluating the safety of stabilised foods.

### **Comments on the effect of oilseed antioxidants on the sensory value of food**

As explained in the preceding paragraph, natural antioxidants from oilseeds should be applied in substantially higher concentrations than the synthetic antioxidants. In such a case, the sensory value of a food product stabilised with oilseed antioxidants may be deteriorated by various off-flavours. They could be tolerable in meat products containing spices, but they would be objectionable in bland products. If heavy metals are present in the extracts, metal chelating synergists, such as citric acid, phospholipids, or phosphoric acid will need to be added to the food preparations. Their acid taste will be perceptible. The adverse effect of some preparations on the sensory value of the stabilised products would decrease the sensory value. The value could be improved by the addition of spices or formation of Maillard products.

### **Comments on technological aspects of application**

The possible application of an additive based on oilseed antioxidants depends on the type of the food products to be stabilised. The direct application of ground oilseeds is possible, and would not be difficult in bakery or with meat products, where the presence of spices could mask the eventual off-flavours. The application of expeller cakes, extracted meals or extracts obtained by extraction with organic solvents is possible, best in the case of bakery, meat, dairy, or potato products, especially in the case of oilseeds often consumed, such as soybeans or peanuts.

The application of oilseed antioxidants to animal fats or edible oils is doubtful because of the formation of cloudiness, with the exception of tocopherol concentrates. The cloudiness is due to the insoluble polar antioxidants as their solubility in bulk fats and oils is lower than the efficient concentration. The undissolved particles should be removed by filtration which would increase the cost.

### **Availability of oilseed antioxidant preparations**

The regular availability of an additive on the market is very important for the food manufacturer. The preparations of oilseed antioxidants are not easily available on the market, but they can

be easily prepared from extracted oilseed meals, particularly from soya beans or sesame seeds. Deodorisation condensates in crude oil processing are a ready source of tocopherols. They can be still more concentrated by fractionation in acetone at  $-70^{\circ}\text{C}$  (NOGALA-KAŁUCKA *et al.* 2004). Solvent extracted preparations from extracted meals would be probably available without a great difficulty in the case of interest, but the producer would hesitate if the orders were not guaranteed for a long time ahead. On the contrary, the oil processor willd hesitate to start with food stabilisation using antioxidant preparations, if there is no former experience with the preparation and its availability is not guaranteed.

#### **Comments on the price of food stabilisation with oilseed antioxidants**

The price of the antioxidants from oilseeds are difficult to predict as they would depend from the volume of the production and from the agricultural conditions of the particular year. From the standpoint of price, the direct application of ground oilseeds would be surely advantageous, but they are acceptable only in the bakery (e.g. in case of sesame seeds) and meat products, usually in combination with spices. Extracted meals are relatively cheap, and the concentration of polar antioxidants in them is higher than in oilseeds. Still, the con-

centration of antioxidants is much lower than in herbs and spices so that high additions would be necessary in the case of oilseeds. Therefore, the yields during the isolation of active extracts would be lower, and the product would be more expensive than in the case of preparations from leaves and herbs. The extracts obtained from extracted meals by subsequent extraction with organic solvents would be more active than the original extracted meals, however, higher amounts will be necessary compared to synthetic antioxidants. Therefore, these purified preparations could be used only in special food products where the price does not play any significant role, such as functional and dietary foods or nutraceuticals.

#### **Comparison of advantages and disadvantages of natural antioxidants from oilseeds and synthetic antioxidants**

Natural antioxidants from oilseeds and synthetic antioxidants permitted by authorities are compared (Table 3) from different aspects. It is evident from the comparison that both types of antioxidants posses both advantages and disadvantages. It is necessary to examine the particular application in the food product studied from all aspects, not only from the aspect of antioxidant activity, and to confirm the conclusion by experiment. Natural antioxidants from

Table 3. Comparison of oilseed antioxidants and synthetic antioxidants

Advantages and disadvantages of oilseed antioxidants	Advantages and disadvantages of synthetic antioxidants
As they are natural substances, they are readily accepted by most consumers	As they are synthetic chemicals, they are suspect to most consumers
Addition of extracts and concentrates is possible, no need of pure substances	They are chemically defined substances of known composition
Contents of antioxidants and accompanying substances are very variable	Their properties are constant, impurities are present only in traces
Raw materials are readily available and cheap, but purified extracts are expensive, and the price may differ according to the crop	All antioxidants are available at relatively low prices
Raw materials are considered as safe, but the safety of pure substances is not assured	Synthetic antioxidants are harmless at levels specified in the regulations
The number of oilseeds which could be used is large, even when only a few are readily available	Only small number of substances is permitted, but in combination with synergists, they usually meet all requirements of producers
They are sensorically neutral or acceptable at low concentrations, but problems may arise at concentrations guaranteeing the activity	They are sensorically neutral at concentrations permitted by regulations

herbs, leaves, spices, or cereal brans are available, too, and may be preferred to natural antioxidants from oilseeds in the majority of cases.

### Conclusions

1. Oilseeds contain lipophilic antioxidants, mainly tocopherols, which are extracted during oilseed processing. The antioxidants can be obtained from deodorisation sludges obtained during crude oil refining. Tocopherols are useful and efficient in the stabilisation of food products of animal origin.
2. Oilseed cakes and extracted meals still contain, after the removal of nonpolar antioxidants, antioxidants of medium or high polarity, mainly phenolic acids, their esters, flavonoids and their glycosides, or lignan derivatives. They possess moderate antioxidant activities, nevertheless, they could be applied with success in special foods.
3. Advantages and disadvantages of phenolic oilseed antioxidants are compared with those of synthetic antioxidants. No general rule can be established for the preference. The most suitable antioxidants should be selected in every particular case after consideration of all aspects, i.e. not only the activity, but also their effects on the product properties, availability, safety and price.

### References

- AMAROWICZ R., SHAHIDI F. (1994): Application of Sephadex LH-20 chromatography for the separation of cyanogenic glycosides and hydrophilic phenolic fraction from flaxseed. *Journal of Liquid Chromatography & Related Technologies*, **17**: 1291–1299.
- AMAROWICZ R., WANASUNDARA U.N., SHAHIDI F. (1994): Chromatographic separation of flaxseed phenolics. *Nahrung/Food*, **38**: 520–526.
- AMAROWICZ R., WANASUNDARA U.N., KARAMAC M., SHAHIDI F. (1996): Antioxidant activity of ethanolic extract of mustard seed. *Nahrung/Food*, **40**: 261–263.
- AMAROWICZ R., RAAB B., KARAMAC M. (1999): Antioxidative activity of an ethanolic extract of evening primrose. *Nahrung/Food*, **43**: 216–217.
- AMAROWICZ R., NACZK M., SHAHIDI F. (2000): Antioxidant activity of crude tannins of canola and rapeseed hulls. *Journal of the American Oil Chemists' Society*, **77**: 957–961.
- AMAROWICZ R., FORNAL J., KARAMAC M., SHAHIDI F. (2001): Antioxidant activity of extracts of phenolic compounds from rapeseed oil cakes. *Journal of Food Lipids*, **8**: 65–74.
- ARAI S., SUZUKI H., FUJIMAKI M., SAKURAI Y. (1966): Flavour compounds in soybean. II. Phenolic acids in defatted soybean flour. *Agricultural and Biological Chemistry*, **30**: 364–369.
- BERGER K. (1998): Edible oil innovations reviewed. *INFORM*, **9**: 785–786.
- BOSKOU D. (1996): Olive oil composition. In: *Olive Oil Chemistry and Technology*. AOCS Press, Champaign, IL: 52–83.
- BOSKOU D., MORTON I.D. (1976): Effect of plant sterols on the rate of deterioration of heated oils. *Journal of the Science of Food and Agriculture*, **27**: 928–932.
- BRENES M., HIDALGO F.J., GARCÍA A., RIOS J. J., GARCÍA P., ZAMORA R., GARRIDO A. (2000): Pinoresinol and 1-acetoxypinoresinol, two new phenolic compounds identified in olive oil. *Journal of the American Oil Chemists' Society*, **77**: 715–720.
- BUDOWSKI P. (1950): Sesame oil. III. Antioxidant properties of sesamol. *Journal of the American Oil Chemists' Society*, **27**: 264–267.
- CINQUANTA L., ESTI M., DiMATTEO M. (2001): Oxidative stability of virgin olive oils. *Journal of the American Oil Chemists' Society*, **78**: 1197–1202.
- DABROWSKI K.J., SOSULSKI F.W. (1984): Composition of free and hydrolyzable phenolics acids in defatted flours of ten oilseeds. *Journal of Agricultural and Food Chemistry*, **32**: 128–130.
- DACHTER M., VAN DE PUT F.H.M., VAN STIJN E., BEINDORFF C.M., FRITSCHÉ J. (2003): On-line LC-NMR-MS characterization of sesame oil extracts and assessment of their antioxidant activity. *European Journal of Lipid Science and Technology*, **105**: 488–496.
- DELEONARDIS A., MACCIOLA V., DiDOMENICO N. (2005): A first pilot study to produce a food antioxidant from sunflower seed shells. *European Journal of Lipid Science and Technology*, **107**: 220–227.
- FAESEL P. (1998): Recent developments and improvements in palm oil stripping and fatty acid distillation. In: LEONARD E.C., PERKINS E.G., CAHN A. (eds): *Proceedings World Conference Palm Coconut Oils for the 21<sup>st</sup> Century*. AOCS Press, Champaign, IL: 67–72.
- FILS J.-M. (2000): The production of oils. In: HAMM W., HAMILTON R.J. (eds): *Edible Oil Processing*. Sheffield Academic Press, Sheffield, UK: 47–78.
- FIRESTONE D. (1996): *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 4<sup>th</sup> ed. AOCS Press, Champaign, IL.
- FRANKEL E.N. (1993): In search of better methods to evaluate natural antioxidants and oxidative stability in food lipids. *Trends in Food Science & Technology*, **4**: 220–225.
- FUKUDA Y., NAGATA M., OSAWA T., NAMIKI M. (1986a): Chemical aspects of the antioxidative activity of roasted



- sesame oil, and the effect of using the oil for frying. *Agricultural and Biological Chemistry*, **50**: 329–340.
- FUKUDA Y., NAGATA M., OSAWA T., NAMIKI M. (1986b): Contribution of lignan analogs to antioxidative activity of refined unroasted sesame seed oil. *Journal of the American Oil Chemists' Society*, **63**: 1027–1031.
- FULEKI T., DASILVA J.M.R. (1997): Catechin and procyanidin composition of seeds from grape cultivars grown in Ontario. *Journal of Agricultural and Food Chemistry*, **45**: 1156–1160.
- GENNARO L., PICCIOLI BOCCA A., MODESTI D., MASELLA R., CONI E. (1998): Effect of biophenols on olive oil stability evaluated by thermogravimetric analysis. *Journal of Agricultural and Food Chemistry*, **46**: 4465–4469.
- GOPALA KRISHNA A.G., PRASHANTH P.A., PRAGASAM A., RAGHAVENDRA K.V., KHATOON S. (2003): Unsaponifiable matter and oxidative stability of commercially produced Indian rice bran oils. *Journal of Food Lipids*, **10**: 329–340.
- GUARDIOLA F., DUTTA P.C., CODONY R., SAVAGE G.P. (2002): Cholesterol and Phytosterol Oxidation Products: Analysis, Occurrence and Biological Effects. AOCS Press, Champaign, IL.
- GUPTA M. K., WARNER K., WHITE P.J. (2004): *Frying Technology and Practices*. AOCS Press, Champaign, IL.
- GUTFINGER T. (1981): Polyphenols in olive oils. *Journal of the American Oil Chemists' Society*, **58**: 966–968.
- HEIMANN W., VON PEZOLD H. (1957): Über die pro-oxygene Wirkungen von Antioxygene. *Fette, Seifen, Anstrichmittel*, **59**: 330–332.
- HENNING W. (1982): Rapid determination of sinapine from mustard and mustard oil seeds by paired-ion HPLC. *Zeitschrift für Lebensmitteluntersuchung und -Forschung*, **175**: 345–348.
- HOPPE M. B., JHA H. C., EGGE H. (1997): Structure of an antioxidant from fermented soybeans (tempeh). *Journal of the American Oil Chemists' Society*, **74**: 477–479.
- HRON R.J., KIM H.L., CALHOUN M.C., FISHER G.S. (1999): Determination of (+)-, (–), and total gossypol in cottonseed by high-performance liquid chromatography. *Journal of the American Oil Chemists' Society*, **76**: 1351–1355.
- JAYAPRAKASHA G.K., SINGH R.P., SAKARIAH K.K. (2001): Antioxidant activity of grape seed (*Vitis vinifera*) extracts on peroxidation models *in vitro*. *Food Chemistry*, **73**: 285–290.
- JOHANSSON P., KAMAL-ELDIN A., LUNDGREN L.N., AMAN P. (2000): HPLC method for analysis of secoisolaricresinol diglucoside in flaxseeds. *Journal of Agricultural and Food Chemistry*, **48**: 5216–5219.
- KAMAL-ELDIN A. (2003): *Lipid Oxidation Pathways*. AOCS Press, Champaign, IL.
- KAMAL-ELDIN A., APPELQVIST L.-A. (1996): The chemistry and antioxidant properties of tocopherols and tocotrienols. *Lipids*, **19**: 671–701.
- KARCHESY J.J., HEMMINGWAY R.W. (1986): Condensed tannins: (4 $\beta$ -8; 2- $\beta$ -O-7)-linked procyanidins in *Arachis hypogaea* L. *Journal of Agricultural and Food Chemistry*, **34**: 966–970.
- KOZŁOWSKA H., ZADERNOWSKI R., SOSULSKI F.W. (1984): Phenolic acids of oilseed flours. *Nahrung*, **27**: 449–453.
- KRYGIER K., SOSULSKI F., HOGGIE I. (1982): Free, esterified, and insoluble-bound phenolic acids. 2. Composition of phenolic acids in rapeseed flour and hulls. *Journal of Agricultural and Food Chemistry*, **30**: 334–336.
- LEUNG J., FENTON T.W., CLANDININ D.R. (1981): Phenolic components of sunflower flour. *Journal of Food Science*, **46**: 1386–1388.
- LOU H., YUAN H., MA B., REN D., JI M., OKA S. (2004): Polyphenols from peanut skins and their free radical-scavenging effects. *Phytochemistry*, **65**: 2391–2399.
- MOURE A., FRANCO D., SINEIRO J., DOMÍNGUEZ H., NUÑEZ M.J. (2003): Simulation of multistage extraction of antioxidants from Chilean hazelnut (*Gevuina avellana*) hulls. *Journal of the American Oil Chemists' Society*, **80**: 389–396.
- MURAKAMI H., ASAKAWA T., TERAOKA J., MATSUSHITA S. (1984): Antioxidative stability of tempeh and liberation of isoflavones by fermentation. *Agricultural and Biological Chemistry*, **48**: 2971–2975.
- MURPHY D.J. (1993): Structure and function of oleoresins in plants. *INFORM*, **4**: 922–932.
- MUSHER S. (1936): Stabilizing fats and oils. US pat., 2,049,017.
- NACZK M., AMAROWICZ R., PINK D., SHAHIDI F. (2000): Insoluble condensed tannins of canola/rapeseed. *Journal of Agricultural and Food Chemistry*, **48**: 1758–1762.
- NENADIS N., BOYLE S., BAKALBASSIS E.G., TSIMIDOU M. (2003): An experimental approach to structure-activity relationships of caffeic and dihydrocaffeic acids and related monophenols. *Journal of the American Oil Chemists' Society*, **80**: 451–458.
- NIKLOVÁ I., SCHMIDT Š., HABALOVÁ K., SEKRETÁR S. (2001): Effect of evening primrose extracts on oxidative stability of sunflower and rapeseed oils. *European Journal of Lipid Science and Technology*, **103**: 299–306.
- NINFALI P., ALUIGI G., BACCHIOCCA M., MAGNANI M. (2001): Antioxidant capacity of extra-virgin olive oil. *Journal of the American Oil Chemists' Society*, **78**: 243–247.
- NOGALA-KAŁUCKA M., KORCZAK J., WAGNER K.-H., ELMADFA I. (2004): Tocopherol composition of deodorization distillates and their antioxidative activity. *Nahrung*, **48**: 34–37.

- OOI G.K., CHOO Y.M., MA A.N. (1996): Refining of red palm oil. *Elaeis*, **8**: 20–28.
- PACKER L. (1996): Antioxidant defenses in biological systems. In: PACKER L., TRABER M.G., XIN W. (eds): *Proceedings International Symposium On Natural Antioxidants*. AOCS Press, Champaign, IL: 9–23.
- PACKER L., ONG A.S.H. (1998): *Biological Oxidants and Antioxidants: Molecular Mechanisms and Health Effects*. AOCS Press, Champaign, IL.
- PAIVA-MARTINS F., GORDON M.H. (2002): Effects of pH and ferric ions on the antioxidant activity of olive polyphenolics in oil-in-water emulsions. *Journal of the American Oil Chemists' Society*, **79**: 571–576.
- PALOZZA P., KRINSKY N.I. (1992): Antioxidant effects of carotenoids *in vivo* and *in vitro*. *Methods in Enzymology*, **213**: 403–420.
- POKORNÝ J., KORCZAK J. (2001): Preparation of natural antioxidants. In: POKORNÝ J., YANISHLIEVA N., GORDON M. (eds): *Antioxidants in Food*. Woodhead Publishing, Cambridge, UK: 311–330.
- PRATT D.E., BIRAC P.M. (1979): Source of antioxidant activity of soybeans and soy products. *Journal of Food Science*, **44**: 541–544.
- PRATT D.E. (1984): A flavonoid antioxidant in Spanish peanuts (*Arachis hypogaea*). *Journal of the American Oil Chemists' Society*, **61**: 1064–1067.
- RICKARD S.E., THOMPSON L.U. (1997): Health effects of flaxseed mucilage lignans. *INFORM*, **8**: 860–865.
- ROVELLINI P., CORTESI N. (2003): Determination of phenolic compounds in different cultivars during olive drupe refining by LC-MS. *Olivae*, **95**: 3238.
- SABIR M.A., SOSULSKI F.W., KERNAN J.A. (1974): Phenolic constituents in sunflower flour. *Journal of Agricultural and Food Chemistry*, **22**: 572–574.
- SAITO M., HOSOYOMA H., ARIGA T., KATAOKA S., YAMAJI N. (1998): Antiulcer activity of grape seed extract and procyanidins. *Journal of Agricultural and Food Chemistry*, **46**: 1450–1464.
- SCHMIDT Š., NIKLOVÁ I., SEKRETÁR S. (1998): Antioxidačný účinok extraktov z repkových a pupalkových šrotov. *Bulletin potravinárskeho výskumu*, **37**: 257–265.
- SCHMIDT Š., POKORNÝ J., VAJDÁK M., SEKRETÁR S., GORDON M.H. (2003): Oilseeds as a source of antioxidants. *Bulletin potravinárskeho výskumu*, **42**: 133–149.
- SHAHIDI F., AMAROWICZ R., HE Y., WETTASINGHE M. (1997): Antioxidant activity of phenolic extracts of evening primrose (*Oenothera biennis*). A preliminary study. *Journal of Food Lipids*, **4**: 75–86.
- SHAHIDI F., NACZK M. (1995): *Food Phenolics*. Technomic Publishing, Lancaster, PA, Basel, CH.
- TERESA E.B., YOLANDA G.F., JULIAN C.R., CELESTINO S.B. (1992): Characterisation of procyanidins of *Vitis vinifera* var. Tinta del país seeds. *Journal of Agricultural and Food Chemistry*, **40**: 1794–1799.
- TSIMIDOU M., PAPADOPOULOS G., BOSKOU D. (1992): Determination of phenolic compounds in virgin olive oil by reversed-phase HPLC with emphasis on UV-detection. *Food Chemistry*, **44**: 53–60.
- WALTER E.D. (1941): Genistin (an isoflavone glucoside and its aglucon, genistein, from soybeans. *Journal of the American Oil Chemists' Society*, **63**: 3273–3276.
- WANASUNDARA U.N., SHAHIDI F. (1994): Canola extract as an alternative natural antioxidant for canola oil. *Journal of the American Oil Chemists' Society*, **71**: 817–822.
- XU L., DIOSADY L.L. (1997): Rapid method for total phenolic acid determination in rapeseed/canola meals. *Food Research International*, **30**: 571–574.
- XU Z., HUA B., GODBER J.S. (2001): Antioxidant activity of tocopherols, tocotrienols, and  $\gamma$ -oryzanol components from rice bran accelerated by 2,2'-azobis(2-methylpropionylamidine) hydrochloride. *Journal of Agricultural and Food Chemistry*, **49**: 2077–2081.
- ZADERNOWSKI R., NOWAK-POLAKOWSKA H., KONOPKA I. (1996): Effect of heating on antioxidative activity of rapeseed and evening primrose extracts. *Polish Journal of Food and Nutrition Sciences*, **5**: 13–20.

Received for publication December 14, 2004

Accepted after corrections May 23, 2005

---

*Corresponding author:*

Doc. Ing. ŠTEFAN SCHMIDT, Ph.D., Slovenská technická univerzita, Fakulta chemickej a potravinárskej technológie, Katedra potravinárskej technológie, Radlinského 9, 812 37 Bratislava, Slovenská republika  
tel.: + 421 2 593 255 56, fax: + 421 2 524 931 98, e-mail: stefan.schmidt@stuba.sk

---