UDC 577.115:665.372:577.125.33:578.282
ISSN 0352-9193

preliminary communication

Phospholipids as Inhibitors of Oxidation During Food Storage and Frying

Fosfolipidi kao inhibitori oksidacije tijekom skladištenja i prženja hrane

Lenka Kouřimská, J. Pokorný and Zuzana Réblová

Department of Food Chemistry and Analysis, Faculty of Food and Biochemical Technology, Institute of Chemical Technology, Technicka St. 5, CZ-166, 28 Frague 6, Czech Republic

Received: June 17, 1994
Accepted: September 26, 1994

Summary

Soybean or rapeseed lecithin and phospholipid concentrates from the same sources do not substantially affect the sensory value of oils or fried products provided their mass fractions in oil being ≤ 0.05 % and ≤ 0.2 %, respectively. They inhibit the lipid oxidation both under storage conditions at 40 °C and at 150–180 °C, especially during the French frying. They are active as synergists of tocopherols, present in edible oils as minor components. Ascorbyl palmitate enhances the activity of phospholipids. The mechanism of their efficiency is their reaction with lipid hydroperoxides following a non-radical mechanism and as heavy metal chelating agents. They not only suppress the accumulation of hydroperoxides, but they decrease the formation of non-peroxidic oxidation products and polymers as well. The amount of total polar compounds in frying oil is lower in the presence of phospholipids than in their absence when products of the same sensory value are compared.

Sažetak

Sojin ili repičin lecitin i njihovi koncentrati ne utječu bitno na senzorska svojstva ulja ili prženih proizvoda ako su im maseni udjeli u ulju ≤ 0,05 % odnosno ≤ 0,2 %. Oni inhibiraju oksidaciju lipida u uvjetima skladištenja i na 40 °C i na 150–180 °C, a osobito tijekom prženja krumpira. Aktivni su kao singergisti tokoferola prisutnih u jestivim uljima. Askorbilpalmitat pojačava aktivnost fosfolipida. Njihovo djelovanje osniva se na reakciji s hidroperoksidima lipida koja ne slijedi mehanizam radikala te stvaranju helata s teškim metalima. Ne samo da sprečavaju nakupljanje hidroperoksida već povećavaju stvaranje neperoksidnih produkata oksidacije kao i polimera. Udio je ukupnih polarnih sastojaka u ulju nakon prženja niži u prisutnosti fosfolipida ako se uspoređuju proizvodi istih senzorskih svojstava.

Introduction

Phospholipids are natural constituents of the fats and oils of many foods. Generally, they possess moderate antioxidant activity, especially in the presence of phenolic antioxidants and/or acidic synergists. Phospholipids are known to improve the oxidative stability by chelating traces of heavy metals and by decomposing hydroperoxides by means of a non-radical pathway *(1)*. Their antioxidant activity is also due to the reaction of hydroperoxides with nitrogen compounds present in phospholipids with formation of inactive compounds.

In our previous experiments *(2)* we found that natural soybean lecithin with mass fractions of ≤ 0.5 % does not significantly affect sensory and functional properties of the oil, but inhibits the peroxide formation, increases weight, and formation of polar compounds during storage at 40 °C very effectively. This stated concentration even improves the flavour acceptability of rapeseed oil and reduces the level of rancid off-flavour that can developed during storage. The addition of phospholipids was thus favourable, not only from the standpoint of the nutritional quality, but also from that of stability against oxidative rancidity.

The stabilization of frying oils is very difficult under frying conditions for the following reasons: a) The rate of initiation of oxidation reaction is extremely high, causing antioxidants added at an acceptable mass fraction (0.02 %) to be rapidly decomposed, b) Most antioxidants tend to be somewhat volatile under frying conditions, c) Many other degradation reactions occur in frying oil in addition to the oxidation.

On the other hand, fried food is the in-flavour with a sizable portion of consumers in developed countries. The consumption of fried products has increased within the last ten years and frying is considered to be one of the most commonly used cooking procedures in households, restaurants, and industrial food production. As compounds formed in oil during the frying due to oxidation and pyrolytic reaction decrease its nutritional value, it is recommended to check the oil quality regularly and replace it when the mass fraction of total polar compounds has reached 20–28 % and the polymer content has exceeded 10 % *(3)*. The sensory quality of fried products is usually unacceptable above these levels as well.

Monitoring of these changes within frying oil requires reasonably precise laboratory equipment, which would not be used in a household scale. Although one could use simple quick test tubes for checking *(4)*, generally the decision is made to change the oil simply when it begins to foam or its tangible sensory appeal diminishes.

Antioxidants are used as food additives in order to extend the lifetime of frying oil and to inhibit the formation of undesirable compounds. The number of antioxidants applicable at frying conditions is somewhat limited because of the reasons mentioned above. TBHQ (tert. butyl hydroquinone) is relatively non-volatile and moderately active but it is not permitted in many countries. BHT (butyl hydroxytoluene) may be converted into a less volatile hydroxyderivative which may be used in frying oils. Consumer preference for natural additives has encouraged the use of natural antioxidants in the last years *(5)*. The following natural antioxidants may be used: rosemary extract, tea extract, phenolics of olives or Maillard browning products. Phospholipids have been proved to be active in inhibiting the lipid oxidation in storage conditions *(1,6)* and therefore, their use in frying would be welcome, as they are generally regarded as safe.

Material and Methods

In our experiment, olive oil Giralda (Salgado S. A., Andujar, Spain), which is a blend of refined and virgin olive oil, was used for frying. The advantage is its low polyenoic fatty acids content and the presence of natural olive oil antioxidants. Natural lecithin was prepared by degumming of crude soybean oil with water and phosphoric acid (Milo Olomouc a s., Olomouc, Czech Republic). The content of acetone-insoluble compounds was 62 %. French fries were prepared from Eba potatoes.

A household fryer ITT, Model 2801.11 (Belgium) was filled with 2.5 kg of oil before the first frying. Potatoes were peeled and cut into strips 1 × 1 × 5 cm and fried immediately. The oil was preheated to 170 °C, and then used to fry one batch of French fried potatoes for 5 minutes. Eleven batches of potatoes were subsequently fried with the same oil. No replenishment occurred whatsoever. French fries were tasted using no salt or other additives. This procedure was also repeated with oil containing lecithin as an antioxidant.

The amount of lecithin added to oil was carefully selected so that there would be no significant changes in colour, taste and odour of the oil. Our test also required that the tested oil containing lecithin does not foam significantly more than the control oil which did not contain lecithin. After preliminary experimentation, a lecithin mass fraction of 0.1 % was selected. Lower lecithin concentrations do not have any adverse effects on the sensory characteristics of oil, but are less effective as antioxidants. Lecithin belongs to the group of safety additives (GRAS) and the mass fraction of 0.1 % continues to be acceptable.

Peroxide value of oil during frying was determined iodometrically *(7)* and conjugated double bonds content was determined by ultraviolet spectroscopy *(7)*. HPLC analysis of polymers *(8)* was performed with a Hewlett-Packard 1050 liquid chromatograph and HP 3396 integrator, using PL Gel MIXED-E Column (300 × 7.5 mm), 3 μm, and PL Gel Guard Column, 5 μm purchased from Hewlett-Packard. The mobile phase was tetrahydrofuran, with a flow rate 1.5 min^{-1}, and the detector was a refractive index detector. A calibration plot was determined using tripalmitoylglycerol (Merck AG, Darmstadt, Germany).

Sensory analysis was carried out under standard conditions *(9)* by a group of trained assessors. The flavour acceptability and sensory profile of the French fried potatoes were assessed using unstructured graphical scales with eight descriptors.

Results and Discussion

Fig. 1 shows changes of peroxide value determined in oil after each frying operation. Lecithin has positive effect on suppressing hydroperoxide formation. The peroxide value after 10 fryings increased to approximately 40 mmol kg^{-1}, while in oil containing lecithin it increased to a peroxide value of only 10 mmol kg^{-1}.

During the frying process, hydroperoxides with conjugated system of double bonds were formed as a result of oxidation of linoleic and linolenic acids. The measurement of these conjugated diene groups can therefore be a useful indicator of the extent of oxidation damage.

Changes of conjugated diene compounds are shown in Fig. 2. The content of the diene groups in oil that was used without lecithin was shown to increase regularly after the induction period (after three fryings). However, the diene groups in oil with lecithin showed almost no increases in content during ten fryings.

Polymers, especially dimers, are considered to be the antinutritional compounds with toxicities that have been

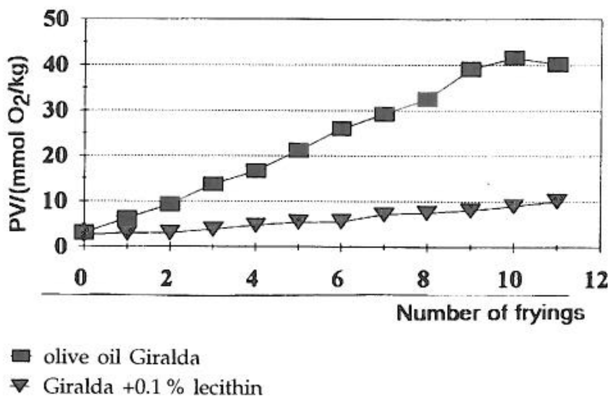

Fig. 1. Changes of peroxide value (PV) during frying
Slika 1. Promjene peroksidnog broja (PV) tijekom prženja

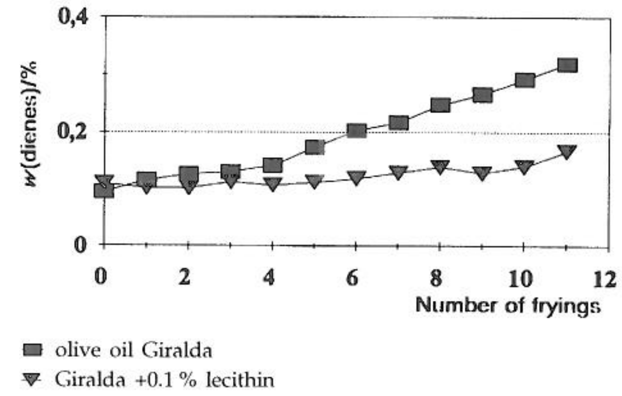

Fig. 2. Changes of conjugated diene compounds during frying
Slika 2. Promjene masenog udjela konjugiranih diena tijekom prženja

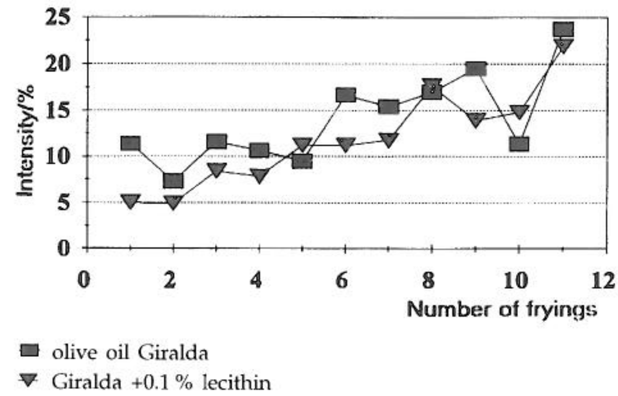

Fig. 4. Rancid off-flavour intensity changes during frying
Slika 4. Promjene intenziteta užegnutosti tijekom prženja

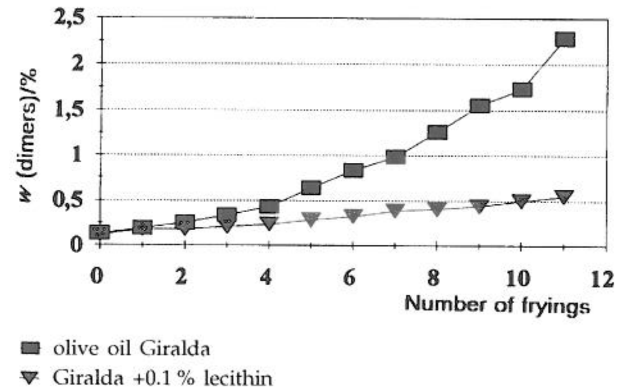

Fig. 3. Changes of dimer content during frying
Slika 3. Promjene masenog udjela dimera tijekom prženja

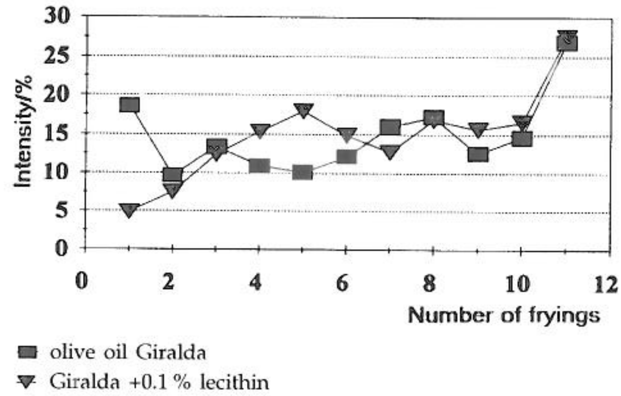

Fig. 5. Intensity of overall off-flavour changes during frying
Slika 5. Intenzitet ukupnih senzorskih promjena tijekom prženja

known for several years *(10,11)*. The dimer content is usually higher than the level of other oligomers.

Changes of dimer content are shown in Fig 3. The influence of the addition of lecithin is the most significant here. The dimer mass fraction was over 2 % in the control oil, but it reached only 0.5 % in oil with lecithin. The dimerization in more unsaturated oils (rapeseed, sunflower seed) could be assumed to be even faster than in olive oil.

High sensory quality and a corresponding strong fried taste is usually required in most fried foods. The reduction of oxidation that resulted from the addition of lecithin most clearly manifested itself in a decrease of rancid and overall off-flavours during our sensory analysis. Consumers are generally quite sensitive to such tastes, and it is therefore very necessary to test for this.

Fig. 4 displays changes in the intensity of rancid off-flavour. There appear to have been no systematic or substantial differences between oils of the two series. The addition of lecithin did not influence the sensory quality of French fries at all. The intensity of rancid off-flavour increased very slowly and the final difference of 10 % is negligible.

There are minimal differences in intensity of overall off-flavours between oils of the two series as well (Fig. 5). The assumption that nitrogen compounds from lecithin could react with oxidation products and form compounds with undesirable odour was not confirmed. The intensity of overall off-flavour of French fries was nearly the same for the whole frying period and did not exceeded 10 %.

Conclusion

Small additions of lecithin (0.1 %) do not reasonably increase the foaming of oil and do not exhibit noticeable effect on the quality of prepared French fries.

French fries prepared in oils with and without lecithin do not differ in acceptability and sensory profile, particularly in regards to rancidity and overall off-flavour.

The addition of lecithin positively suppresses the content of antinutrient compounds in oil such as hydroperoxides, unsaturated fatty acids with conjugated double bonds or dimers. From this point of view, the addition of 0.1 % of lecithin can be recommended.

References

1. Pokorný, Z. Réblová, M. Ranný, J. Káňová, J. Pánek, J. Davídek, *Nahrung, 36* (1992) 461–465.
2. Kouřimská, Z. Réblová, J. Pokorný, Stabilization of dietetic oils containing phospholipids against oxidative rancidity. *6th International Colloquium on Phospholipids, Hamburg* (1993).
3. Márquez-Ruiz, M. C. Pérez-Camino, M. C. Dobarganes, *Grasas Aceites*, 41 (1990) 432–439.
4. Farníková, Z. Réblová, J. Pokorný, Rychlé metody sledováni změn tuku při smažení. *XXXII. seminář z technologie a analytiky tuků, Liblice* (1994).
5. Pokorný, *Trends Food Sci. Technol. 2* (1991) 223–227.
6. Pokorný, J. Davídek, M. Vierecklová, M. Ranný, J. Sedláček, *Nahrung*, 34 (1990) 719–725.
7. IUPAC: *Standard Methods for the Analysis of Oils, Fats and Derivatives*, 7th ed., C. Paquot, A. Hautfenne (Eds.). Blackwell, Oxford (1987).
8. IUPAC, *Pure & Appl. Chem., 8* (1991) 1163.
9. ISO 6658–1985: *Sensory Analysis – Metodology – General Guidance*, International Organization for Standardization, Geneve (1985).
10. R. Matsuo, *Bull. Seikei Univ., 1* (1961) 1–6.
11. Heide, J. Veen, *Voeding, 38* (1977) 406–417.