

Frying temperatures and minor constituents of oils and fats

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SUMMARY

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Two important classes of minor constituents of oils and fats are tocopherols and sterols. Both these classes are biologically active and they also affect the stability and performance of an oil at elevated temperatures. Tocopherols are phenolic antioxidants that react with free radicals and their concentration is reduced significantly when the oil is heated. α -Tocopherol is lost faster during deep-fat frying than the beta, gamma and delta homologues. In the presence of stronger antioxidants, natural or synthetic, losses of α -tocopherol can be eliminated. Unchanged phytosterols naturally present in vegetable oils are believed to be beneficial for the health. Depending on the chemical structure, phytosterols may act as prooxidants or antioxidants. Sterols with an ethylidene group in the side chain have been found effective in retarding polymerisation at temperatures similar to those of deep-fat frying. Under unfavourable conditions (high temperature, presence of air) oxidation products are formed from sterols and a marked increase in the oxidation rate of the fat is observed. Oxidation products of the main phytosterols, β -sitosterol and stigmasterol, are: hydrocarbons (3,5-diene and 3,5,22-triene), mono-, di- and triunsaturated ketosteroids (4-en-3-one, 3,5-dien-7-one, 3,5,22-trien-7-one), 5,6-epoxy derivatives, 3,7-diols and pregnane derivatives. Other minor constituents which may affect the rate of degradation of unsaturated triacylglycerols at high temperatures are squalene, pigments and

phospholipids. Squalene and phospholipids have both been reported to retard the degradation of unsaturated fatty acids under simulated frying conditions. High chlorophyll levels were found to increase the rate of tocopherol decomposition and formation of polymers in rape seed oil heated at 180°C.

KEY-WORDS: *Heated fats – Minor constituents – Sterols – Tocopherols.*

The effect of oxygen on lipids has been extensively studied but most of the research work focuses on triacylglycerols. There is scant information concerning the minor constituents of oils and fats and their decomposition products which may affect the nutritive value and the performance of an oil at high temperatures.

Important classes of the non-glyceridic part of natural fats are tocopherols, sterols, hydrocarbons and pigments. Some of these components are biologically active and their changes during frying cannot be ignored. Health benefits attributed to two important classes of minor constituents of natural fats, tocopherols and sterols, are listed in Table I.

Table I
Health benefits attributed to dietary tocopherols and sterols

Class	Beneficial effect	References
Tocopherols	Hypocholesteremic effect, anticancer effect, prevention of oxidation of low density lipoproteins and myocardial ischemia reperfusion injury.	Esterbaner, 1989, Packer, 1991, Thurnham, 1992, Covian, 1994
Plant sterols	Effect on the absorption of dietary and endogenous cholesterol.	Subbiah, 1973, Mattson, 1977
	Inhibition of tumor development and reduced risk of colon carcinogenesis (non conclusive results).	Jenezic, 1992

While unchanged phytosterols are rather beneficial for the diet, their oxidation products may have detrimental biological effects, as this is

the case with cholesterol. Adverse effects of oxidation products of cholesterol and phytosterols are presented in Table II.

Table II
Detrimental biological effects exhibited by oxidation products of sterols

Class	Effect	References
Cholesterol oxides, epoxycholesterol, various oxidation products of cholesterol	Arterial wall injury-cancer-inhibition of DNA synthesis-mutagenicity	Taylor, 1979, Smith, 1979, Imai, 1980, Sevanian, 1984, Morin, 1991
β -sitosterol epoxides	Scant information Health implications are mainly hypothetical. Assumptions are based on similarities in the chemical structure of β -sitosterol and cholesterol. However, the restricted absorption of β -sitosterol by the human body may mean a restricted also absorption of β -sitosterol oxidation products. Biomedical significance of oxidized β -sitosterol remains to be determined.	Daly, 1983, Finocchiaro, 1983

TOCOPHEROLS

Tocopherols are important primary antioxidants; besides their *in vitro* activity they are also considered to be highly efficient radical quenchers which protect membranes against damage and support normal biological activity.

The postulated mechanism for the *in vivo* formation of dangerous radicals is presented in Figure 1. (Thurnham, 1992). The superoxide radical initially formed is removed by the enzyme superoxide dismutase (catalytic dismutation to hydrogen peroxide). Hydrogen peroxide and lipid hydroperoxides can be removed by glutathione peroxidase. However, in the presence of ferrous ions superoxide radical and hydrogen peroxide interact to produce the hydroxyl radical which is extremely reactive (Aruoma, 1991, Thurnham, 1992). To stop lipid peroxidation the tissues rely on radical quenching antioxidants, principally tocopherols (Langseth, 1995).

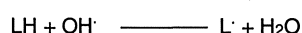
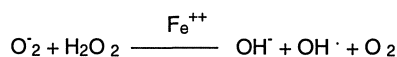
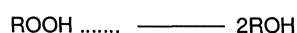
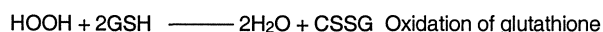
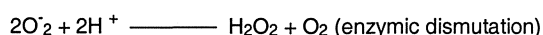
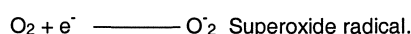


Figure 1
In vivo formation of free radicals and lipid oxidation
(Thurnham, 1992, Langseth, 1995)

Thermal oxidation of tocopherols results in the formation of dimers and trimers (Kiyomi Kikugawa, 1990). Two possible steps in the mechanism of the formation of dimers are the initial formation of

phenoxy radicals and their rearrangement to benzyl radicals. Various types of dimers (biphenylethane, biphenylether, biphenyl type) may be formed. Dimers retain the capacity to act as antioxidants.

Tocopherols as primary antioxidants are consumed during the induction period. Upon heating rapid losses of tocopherols take place and such losses may be used as a measure to monitor the deterioration of frying oils (Kajimoto, 1993, Buchowski, 1995). Gordon and Kourimska (1995) studied the changes in tocopherol content of low erucic acid rapessed oil used for deep fat frying of potatoes. A reduction of approximately 50% was found after 6-8 frying operations. In the presence of added natural antioxidants such as rosemary extracts or ascorbyl palmitate a reduced rate of tocopherol loss was observed. This effect was more pronounced for α -tocopherol which is lost more rapidly at frying temperatures (Table III). An increased stability of the same oil was also reported by Pazola *et al.* (1986) who added rosemary to the dried potato crisps. Rosemary and other herbs of the Lamiaceae family contain antioxidants (Nakatami, 1994) which obviously have a marked stabilising effect on the oil and reduce the rate of loss of tocopherols.

Table III
Change in tocopherol content during frying of potato chips in rapeseed oil. (Gordon, 1995)
(t_{1/2} number of frying operations before the tocopherol level falls by 50%)

Sample	t _{1/2}		
	α -tocopherol	β -tocopherol	γ -tocopherol
Rapeseed oil	4-5	7	7-8
Rapeseed oil and rosemary extract (0.1%)	9-10	11	12
Rapeseed oil and ascorbyl palmitate (0.02%)	8	10	10-11

STEROLS

From the various sterols, cholesterol has been extensively studied, as far as oxidation is concerned. Cholesterol is the principal sterol of higher animals, but it occurs also in plant lipids in small amounts. In the seed oils of Solanaceae e.g. in tomato seed oil, cholesterol is a major sterol (Kiosseoglou, 1989). So far, more than 60 oxidation products of cholesterol have been identified in foodstuffs. The major ones include (Finocchiaro, 1983, Daly, 1983) 25-hydroxy-cholesterol, 5,6 α - and 5,6 β -epoxides, cholest-4-ene-3,6 dione, cholest-5-en-3-one, cholest-4-en-3-one, 7 α - and 7 β -hydroxycholesterol, 7-ketocholesterol and cholest-3,5-diene-7-one. The two epimeric 7 α - and 7 β -diols, were identified in tallow heated at 180°C for an extended period (Ryan, 1981).

β -sitosterol is the predominant and most widely distributed phytosterol. Nourooz-Zadeh and Appelqvist (1992) tried to isolate and determine sterol oxides in crude soybean oil, refined and deodorized soybean oil and fresh olive oil. They failed to detect any oxidation products (for the detection limit of 0.2 ppm). The sterol was also found stable during prolonged storage of soybean oil at 4°C.

Oxidation of β -sitosterol at high temperatures in a model lipid system was studied by Yanishlieva and Schiller (1983). These two authors reported that when the compound is heated in a triacylglycerol system the proportion of non polar oxidation products is higher compared to that observed during heat oxidation of pure β -sitosterol. Oxidation products of β -sitosterol such as α - and β -epoxides and 7 α - and 7 β -hydroxysterols were reported to be present in french fries (Lee, 1985).

Table IV
Structure and concentration of some of the products formed during heating of glycerol tristearate containing 5% β -sitosterol at 120°C (Yanishlieva, 1983)

Structure	% of total sterols
stigmasta-3,5-diene	4.1
stigmasta,3,5-dien-7-one	9.4
stigmast-4-en-3-one	4.2
stigmast-4,6-dien-3-one	4.6
6 β -hydroxy-stigmast-4-en-3-one	4.7
5 α , 6 α and 5 β , 6 β -epoxy-sitosterol	11.8
stigmast-5-ene-3 β , 7 β -diol	5.9
stigmast-5-ene-3 β -7 α -diol	4.4
α 5-stigmasta-3 β , 5 β , 6 β -triol	2.3

Oxidation of stigmasterol in heated triacylglycerols was studied by Blekas and Boskou (1989). A triacylglycerol mixture containing 5% stigmasterol by weight and devoid of other unsaponifiables was heated at 180 \pm 5°C for several hours. Oxidation products from stigmasterol were separated and isolated by column chromatography and preparative thin-layer chromatography. Characterization of individual compounds was based on chromatographic mobilities, specific colour reactions, UV and IR spectroscopy and fragmentation patterns from the mass spectra of the purified oxidation products. A hydrocarbon (stigmasta-3,5,22-triene), a triunsaturated ketosteroid (stigmasta-3,5,22-trien-7-one), a diunsaturated ketosteroid (stigmasta-4,22-diene-3-one) and a pregnane derivative (Δ^5 -pregnen-3 β -ol-20-one) were tentatively identified. There was also evidence for the presence of more polar compounds such as 7-hydroxy sterols, 5,6 - epoxides and Δ^{22} - stigmasten - 3,5,6 triol. Based on existing literature for cholesterol (Fioriti, 1967, Van Lier, 1970, Teng, 1973, Kulig, 1974, Homberg, 1975, Smith, 1978). Blekas (1989) proposed a series of possible reactions for the formation of oxidation products of stigmasterol, both from rings A and B and the side chain.

Effect of sterol on the rate of oxidation of lipid systems at high temperatures

The heat stability of oils and fats depends not only on their fatty acid composition but also on the presence of non-glyceridic constituents such as sterols. 4-Desmethylsterols and 4-methylsterols with an ethylidene group in the side chain as well as their esters have been found to be effective in stabilizing oils at temperatures similar to those reached in deep fat frying. Δ^5 -avenasterol and citrostadienol possess this structural feature and can retard polymerization of oils heated at frying temperatures. (Sims 1972, Boskou 1976, Gordon 1983, Blekas 1986, White 1986, Tian 1994). A hypothesis has been proposed by Gordon (1983) to explain this antipolymerisation effect. Lipid free radicals react rapidly with sterols having unhindered allylic carbon atoms such as in the ethylidene group. Isomerisation produces a stable allylic tertiary free radical which interrupts the oxidation chain reactions.

This effect of natural ethylidene side chain sterols at high temperatures is important since commercially used antioxidants such as tocopherols and synthetic phenols are heat sensitive or volatile. Other sterols without an ethylidene group in the side chain have been shown to have an adverse or no effect. (Sims, 1972, Boskou, 1976, Yanishlieva, 1983, White, 1986, Kajimoto, 1993).

OTHER MINOR CONSTITUENTS

Information related to other minor constituents is very limited. Kourimska, Pokorny and Reblova (1994) studied the effect of phospholipids on heated olive oil. They found that lecithin added at a 0.1% level reduced significantly the concentration of polymers when potatoes were fried at 170°C. Oxidative polymerisation was also found to be retarded by squalene (Sims 1972, Malecka, 1991). Fats tested were safflower and rapeseed oil at 180°C and 170°C, resp. Degradation of rapeseed oil at 180°C was also tested in relation to chlorophyll levels (Murui Tateo, 1993). The rates of decomposition of tocopherols and formation of polymerised oil were higher in oils containing more chlorophyll. This was attributed to prooxidants formed more readily in the oils obtained from high chlorophyll rapeseed.

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