B – Natural Biologically-active Components in Food Raw Materials of Plant and Animal Origin

Heating of Plant Oils – Fatty Acid Reactions *versus* Tocopherols Degradation

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Abstract: Relationship between polymerised triacylglycerols formation and tocopherols degradation was studied during heating of four commercially accessible vegetable oils (rapeseed oil, classical sunflower oil, soybean oil and olive oil) on the heating plate with temperature 180°C. The content of polymerised triacylglycerols 6% (i.e. half of maximum acceptable content) was achieved after 5.3, 4.2, 4.1, and 2.6 hours of heating for olive oil, soybean oil, rapeseed oil and sunflower oil, respectively, while decrease in content of total tocopherols to 50% of the original content was achieved after 3.4, 1.6, 1.3, and 0.5 hours of heating for soybean oil, rapeseed oil, sunflower oil and olive oil, respectively. Because of the high degradation rate of tocopherols, decrease in content of total tocopherols to 50% of the original content was achieved at content of polymerised triacylglycerols 0.6%, 1.9%, 2.8% and 4.9% for olive oil, rapeseed oil, sunflower oil and soybean oil, respectively, i.e. markedly previous to the frying oil should be replaced.

Keywords: tocopherols; frying; polymerised triacylglycerols

INTRODUCTION

The best way to follow the changes of plant oils running during frying is determination of polymerised triacylglycerols (TAG). In this case, changes of the present fatty acids are monitored, whereas the maximum acceptable content of polymerised triacylglycerols is 12% (Anonymous 2000). However, the tocopherols (vitamin E) are destroyed during frying in large measure, too. Though this fact is known and documented in literature (Eitenmiller & Lee 2004), it is not taken into account in other areas of the food science and practice. For example, vitamin E losses coming during frying are not mentioned as part of the recommendations for the frying oil selection (Gupta 2004) and tocopherols are perceived as antioxidants able to protect oil (fatty acids) during frying first of all (Warner *et al*. 2004). Similarly, there is sufficiency of reliable results documenting content of tocopherols in different food raw materials and unprocessed foodstuffs in literature and similar sources, but results describing this for heat-treated foodstuffs are not enough and existing data should be used with caution (Eitenmiller & Lee 2004). Therefore, for assessment of a dietary intake of tocopherols, the results obtained from food composition tables can be overestimated beside the results obtained by diet analysis (Rodríguez-Palmero *et al.* 1998).

With respect to previous, the aim of this work was to describe the relationship between the polymerised triacylglycerols formation and tocopherols (vitamin E) degradation during heating of common (commercially accessible) vegetable oils.

MATERIAL AND METHODS

Plant oils. The tested vegetable oils were purchased in ordinary shops. The rapeseed oil, sunflower oil and soybean oil were fully refined, while

Table 1. Characterisation of the studied vegetable oils

Oil	Rapeseed	Sunflower	Olive	Soybean
Polymerised triacylglycerols (%)	0.31	0.92	0.37	0.40
Total tocopherols (mg/kg)	571	552	225	1067
α-Tocopherol (mg/kg)	265	512	213	136
Vitamin E (α-T equivalents) (mg/kg)	295	525	215	213
Saturated fatty acids (%)	7.8	12.8	16.4	16.4
Monoenoic fatty acids (%)	64.6	25.9	73.4	25.5
Linoleic acid (%)	20.1	59.5	9.5	51.3
Linolenic acid (%)	5.2	0.1	0.5	6.1

the olive oil was the mixture of refined and virgin oils. The input characteristic of the tested oils is summarised in Table 1.

Experiments. The oils samples (25 g ± 1%) were heated in the beakers (volume 100 ml, internal diameter 47 mm) on the heating plate (Präzitherm PZ 28-2, Gestigkeit) with temperature 180°C (± 1°C) for 1–8 hours. Under these conditions, the oils temperature grew 20 min and then fluctuated at interval 154–156°C. Three experiments were realised with everyone oil studied.

Analytical methods. Tocopherols were determined using a reverse phase HPLC with an amperometric detector, fatty acids composition using a gas chromatography and polymerised triacylglycerols using a high performance size exclusion chromatography (HP-SEC).

RESULTS AND DISCUSSION

The studied oils lifetime (calculated using linear regression analysis like time till content of polymerised triacylglycerols 12% was achieved) increased in the order sunflower oil, soybean oil, rapeseed oil and olive oil (5.4, 7.5, 8.0 and 9.7 h, respectively), while period till content of polymerised TAG 6% was achieved (i.e. half of maximum acceptable content, calculated using the two nearest values) increased in the order sunflower oil, rapeseed oil, soybean oil and olive oil (2.6, 4.1, 4.2 and 5.3 h, respectively).

Like parameter comparing the tocopherols degradation in different oils, the time before decrease in content of tocopherols to 50% of the original content was achieved was selected. For total tocopherols, this period increased in the order olive oil, sunflower oil, rapeseed oil and soybean oil (0.5, 1.3, 1.6 and 3.4 h, respectively). The same order was obtained for vitamin E content (0.5, 1.2. 1.3, and 2.4 h, respectively). For α-tocopherol, this period was 0.5, 1.2, 1.2, and 2.0 h for olive oil, sunflower oil, rapeseed oil and soybean oil, respectively.

Because of the high degradation rate of tocopherols, decrease in content of total tocopherols to 50% of the original content was achieved at content

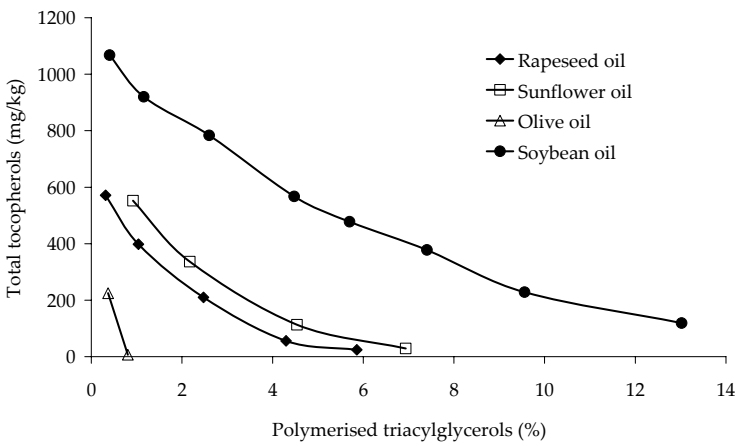

Figure 1. Degradation of tocopherols during heating of the plant oils as function of the polymerised triacylglycerols content

of polymerised triacylglycerols 0.6%, 1.9%, 2.8% and 4.9% for olive oil, rapeseed oil, sunflower oil and soybean oil, respectively, i.e. markedly previous to the frying oil should be replaced. The same order was obtained for vitamin E content and for α-tocopherol content. Decrease in vitamin E content to 50% of the original content was achieved at content of polymerised triacylglycerols 0.6%, 1.4%, 2.8% and 3.3%, while decrease in α-tocopherol content to 50% of the original content was achieved at content of polymerised triacyglycerols 0.6%, 1.3 %, 2.7% and 2.7% for olive oil, rapeseed oil, sunflower oil and soybean oil, respectively.

At the end of oils lifetime (i.e. at content of polymerised triacylgylcerols 12%) no tocopherols were present in the oils studied, except the soybean oil (Figure 1). In the soybean oil (with high natural tocopherols content), content of total tocopherols was 150 mg/kg (i.e. 14% of the original content) at this moment. However, with respect to the high reactivity of α-tocopherol (with the highest biological activity, Eitenmiller & Lee 2004), content of vitamin E was 7.3 mg/kg (i.e. 3.4% of the original content) only and no α-tocopherol was present. Therefore, oils previously used to frying are weak or no source of vitamin E. This agrees with vitamin E content data for the French fries presented by USDA National Nutrient Database (USDA 2008), but higher difference between samples can be expected (in contrast to data listed there).

CONCLUSION

Presented results demonstrate that tocopherols (above all α-tocopherol with the highest biological activity) degrade (markedly or completely) previous to the frying oil should be replaced according to the content of polymerised triacylglycerols. In consideration of the frequent low vitamin E intake (lower than recommended – Maras *et al.* 2004), the tocopherols reactions during frying and similar operations have to be studied and ways able to protect tocopherols should be searched.

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