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Effect of antioxidants on losses of tocopherols during deep-fat frying

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The changes in tocopherol content of oil used for deep-fat frying of potatoes have been studied. It has been found that α-tocopherol is lost much faster than β-, γ- or δ tocopherol, with a reduction of 50% α-tocopherol after 4–5 frying operations compared with values of about 7 and 7–8 frying operations for β- and γ-tocopherol, respectively, in the absence of added antioxidants. However, the presence of a rosemary extract or ascorbyl palmitate in the frying oil caused a marked reduction in the rate of loss of the tocopherols.

INTRODUCTION

Phenolic antioxidants act by reacting with lipid radicals to form relatively stable products which interrupt the propagation stage of the oxidative chain reaction (Gordon, 1990). Hence, the antioxidants are slowly consumed and the end of the induction period corresponds to the time at which the antioxidants have been completely consumed (Dziedzic *et al.*, 1986). Tocopherols are primary antioxidants that behave in this way, but since they also have vitamin E activity it is important that the diet contains sufficient unreacted tocopherols, especially α-tocopherol, which is biologically the most active. The presence of more active primary antioxidants may reduce the losses of tocopherols. Thus, rosemary extract has been shown to retard losses of tocopherols in sardine oil at 30°C (Fang & Wada, 1993). The effect of an extract from rosemary and ascorbyl palmitate on the losses of tocopherols during deep-fat frying has been studied and the results are reported in this paper.

MATERIALS AND METHODS

A commercial extract from rosemary, prepared according to Löliger (1989), was supplied by Food Ingredients Specialities, Hayes, UK and ascorbyl palmitate was purchased from Koch-Light Laboratories, Colnbrook, UK. α-Tocopherol was purchased from Sigma Chemical Co., Poole, UK. Refined low erucic acid natural rapeseed oil was purchased from a local retail outlet.

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An Apex silica, 5 μm HPLC column (25cm × 4·6 mm id) purchased from Jones Chromatography Ltd, Hengoed, UK, was used for tocopherol analysis with a Gilson pump, flow 1 ml min^{-1}, solvent 1·5% isopropanol in hexane, injection volume 20 μl, and a Perkin-Elmer LS-5 fluorescence detector with excitation 290 nm, and emission 330 nm. A Hewlett-Packard 3396A integrator was used for data collection. HPLC calibration curves were plotted with a standard sample of α-tocopherol in the range 2–7 μg ml^{-1}.

Potato chips were prepared by deep frying in rapeseed oil at 162°C on a laboratory scale, and the oil was allowed to cool to room temperature after each frying operation. Twelve batches of potatoes were fried with the oil during a 6-day period and samples were removed for analysis after each frying operation. Fresh oil was not added between batches, and the original oil was used for all frying operations.

RESULTS AND DISCUSSION

Changes in tocopherol concentration during frying of potato chips in rapeseed oil without added antioxidants, and with rosemary extract (0·1%) and ascorbyl palmitate (0·02%) were studied. The antioxidant activity of rosemary extracts has been shown to increase with concentration in the range 0·01–0·1% (Löliger, 1989), and therefore the highest concentration in this range was chosen for addition. The solubility of ascorbyl palmitate is limited to 0·03% in some vegetable oils (Coppen, 1989) and previous work indicates that this antioxidant is effective in stabilising oils at a concentration of 0·02% with only minor increases in antioxidant activity above this level (Gwo *et al.*, 1985), and consequently this concentration was chosen for these studies.

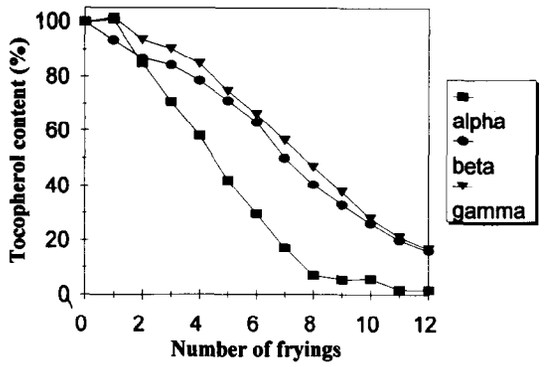

Fig. 1. Relative change in tocopherol content during frying of potato chips in rapeseed oil.

The concentrations of α-, β, γ- and δ- tocopherols in rapeseed oil were found to be 215, 106, 401 and <13 ppm, respectively, based on the α-tocopherol calibration curve and using the same response factor for each tocopherol. This may give a slight overestimate of the concentration of β-, γ- and δ-tocopherol since the response factors relative to α-tocopherol are reported to be 1: 1·29: 1·1: 1.22 (Thompson & Hatina, 1979) or 1: 1·14: 1·18 (α:β:δ) (Duggan, 1959). However, these concentrations are within the range of 180–280, 380–590 and 10–20 ppm reported respectively for α-, γ- and δ-tocopherols in rapeseed oil by Schuler (1990). Rahman (1990) reported 250, 157, 519 and 9 ppm for α-, β-, γ-. and δ-tocopherol, respectively. The δ-tocopherol level was near the limit of detection and therefore changes in this component are not discussed in this paper.

The rapeseed oil with no additives showed clearly that the α-tocopherol was consumed significantly faster than the β- or γ-tocopherol (Fig. 1). This difference in stability of the tocopherols was also evident in the oil samples containing rosemary extract and ascorbyl palmitate (Figs 2 and 3). However, both rosemary extract and ascorbyl palmitate increased the stability of the tocopherols by a considerable extent. A 50% reduction in concentration of α-tocopherol occurred after about 4–5 frying operations for the control compared with values of 9–10 and about 8 for samples fried in rapeseed oil containing the rosemary extract at 0·1% and ascorbyl palmitate at 0·02%, respectively. Similar

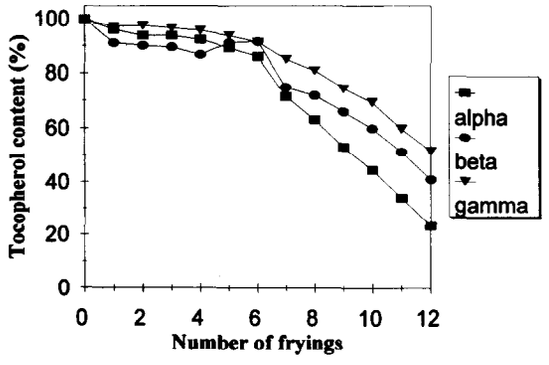

Fig. 2. Relative change in tocopherol content during frying of potato chips in rapeseed oil containing 0·1% rosemary extract.

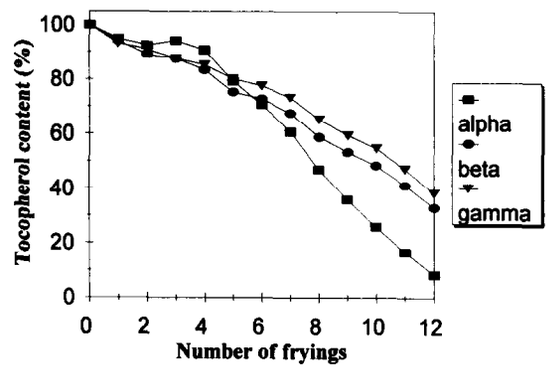

Fig. 3. Relative change in tocopherol content during frying of potato chips in rapeseed oil containing 0·02% ascorbyl palmitate.

Table 1. Number of frying operations before the tocopherol level falls by 50% ($t_{1/2}$)

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

stabilisation of β- and γ-tocopherols was also evident (Table 1).

The stabilising effect of the rosemary extract and the ascorbyl palmitate in reducing losses of α-tocopherol is particularly marked, and it is clear that the rosemary extract was slightly more active than the ascorbyl palmitate at the concentrations used.

The more rapid loss of α-tocopherol compared to the other tocopherols has been observed in previous studies at lower temperatures (Lehmann & Slover, 1976; Cetin, 1989). The present study confirms that α-tocopherol is also lost most rapidly at frying temperatures, and also shows the use of a rosemary extract or ascorbyl palmitate in reducing the rate of loss of tocopherols.

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