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Analytical Methods

Volatile compounds and fatty acid profiles in commercial milk-based infant formulae by static headspace gas chromatography: Evolution after opening the packet

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Abstract

The evolution of the volatile compounds propanal, pentanal and hexanal, and fatty acid profiles were examined in 20 infant formula (IF) milk powders during storage at 25 °C for 70 days after their packaging was opened. Few changes were observed in the fatty acid content during storage, but significant losses were found in C18:2 $n-6$ and C18:3 $n-3$ for some formulae. All three volatiles increased during storage in all formulae, confirming oxidative stability decreases once packets were opened. Significant correlation ($p < 0.05$) was detected between hexanal content and oxidation of $n-6$ PUFA, specifically C18:2 $n-6$ losses, and between propanal content and oxidation of $n-3$ PUFA, specifically from C18:3 $n-3$ losses.

Keywords: Infant formula powders; Volatile compounds; Propanal; Pentanal; Hexanal; Fatty acids

1. Introduction

Lipid oxidation causes quality deterioration during manufacture and storage of lipid-containing foods. In the peroxidation of unsaturated fatty acids, lipid hydroperoxides are formed during the propagation phase. These primary compounds are unstable and rapidly decompose in the presence of trace elements to give a range of compounds, including alkoxyl and alkyl radicals, aldehydes, ketones and a range of carboxyl compounds that form a complex mixture of secondary lipid oxidation products, which spoil infant formula (IF) milk powders. Traditionally, the peroxide value (POV) has been used to determine primary lipid oxidation products, and the thiobarbituric acid (TBA) assay for secondary oxidation products. Several protocols have been described for the determination of POV in milk products (FIL-IDF, 1991; Newstead & Headifen, 1981). However, with complex foods such as IFs, a lipid extraction is required prior to POV measurement and this may introduce error and increase analysis time (Perkins, 1984). In contrast, the TBA test can be applied directly to the sample. However, the appropriateness of the TBA assay, especially when applied to milk and milk products, has been questioned (Ward, 1985). Researchers have focused their efforts on new technologies and methods for the evaluation of food lipid damage, that are simple, fast, reliable and sensitive, requiring less time and with minimal sample treatment.

Direct injection of fat into the heated injection port of a gas chromatograph and quantification of volatile substances originating from the thermal breakdown of lipid peroxides was a widely used approach for measuring rancidity in fatty foods (Dupuy, Fore, & Goldblat, 1973). Later automatic samplers for static or dynamic headspace gas chromatography were used, for the determination of volatile compounds produced by oxidation (Snyder, Frankel, Selke, & Warner, 1988; Ulberth & Roubicek, 1993). The static head space gas chromatography (SHS-GC)

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method reported by Romeu-Nadal, Castellote, and Lopez-Sabater (2004) for IF analysis is an easy, fast and reliable method for determining the main volatile compounds.

Many studies have reported the development of off-flavours in milk at a given storage time, usually at the end of the product's shelf-life (Cormier, Raymond, Champagne, & Morin, 1991; Vallejo-Cordoba & Nakai, 1994; Contarini & Pavolo, 2002). Volatile compounds such as hexanal and pentanal have been associated with the development of undesirable flavours and have been proposed as potential markers of fresh milk quality (Contarini & Pavolo, 2002; Karatapanis, Badeka, Riganakos, Savvaidis, & Kontominas, 2006; Kim & Morr, 1996; Marsili & Miller, 2003; Toso, Procida, & Stefanon, 2002). Concentrations of saturated aldehydes and hydrocarbons correlate well with sensory flavour (Hall & Andersson, 1985; Hall, Andersson, Lingnert, & Olofsson, 1985). A "cardboard-like" off-flavour is frequently associated with dehydrated milk products. This effect is highly correlated with the headspace concentration of hexanal (Hall et al., 1985). In stored UHT milk, concentrations of pentanal and hexanal are also related to the development of off-flavour (Rerkrai, Jeon, & Bassette, 1987). Several sampling techniques are currently available for the isolation and measurement of volatile compounds, such as gas chromatography (GC)–mass spectrometry-based electronic nose, solid-phase microextraction (SPM), GC/mass spectrometry (GC/MS), vacuum distillation, simultaneous steam distillation and extraction GC, static headspace (SHS), dynamic HS/ purge and trap GC, and direct thermal desorption (Cruwys, Dinsdale, Hawkes, & Hawkes, 2002; Contarini & Pavolo, 2002; Fenaille, Visani, Fumeaux, Milo, & Guy, 2003; Hardas, Danviriyakul, Foley, Nawar, & Chinachoti, 2002; Jung, Yoon, Lee, & Min, 1998; Kolb, 1999; Marsili, 1999a; Marsili, 1999b). The SHS technique requires minimal sample treatment and reduces artifactual volatile compound formation.

Many milk-based IF powders are supplemented with polyunsaturated fatty acids, such as arachidonic acid (C20:4, $n-6$) (AA) and docosahexaenoic acid (C22:6, $n-3$) (DHA), which are more susceptible to oxidation than linoleic acid (C18:2, $n-6$) (LA), and may produce undesirable flavours and odours. However, LA is the main polyunsaturated fatty acid in IFs (Ulberth & Roubicek, 1995). The content of hexanal, which is a major breakdown product of LA oxidation (Frankel, 1993), has been used to follow the course of lipid oxidation and off-flavour development in foods (Dupuy et al., 1977). Pentanal and hexanal are volatile oxidation products of $n-6$ PUFA and propanal of $n-3$ PUFA (Romeu-Nadal et al., 2004). In spite of literature related to volatile content in milk (liquid and powdered), information about these compounds in IFs is scarce. van Ruth, Floris, and Fayoux (2005) studied the volatile profiles of 13 IFs by proton transfer reaction-mass spectrometry. Fenaille et al. (2006) measured the levels of secondary lipid oxidation products (malondialdehyde and hexanal) in relation to the processing conditions of IF, pasteurised and UHT milk samples.

When stored, IFs are usually protected from light and maintained at room temperature. However, because of the long storage life of these powders (usually 2 years), PUFAs can be oxidised, giving rise to a loss of nutritive value and to the generation of volatile compounds from peroxides. UV light induces lipid oxidation, therefore milk products such as IFs, once opened, are highly susceptible to lipid oxidation at room temperature, and light accelerates this process (Hardas, Danviriyakul, Foley, Nawar, & Chinachoti, 2000). There is a lack of information on the concentration and evolution of volatile compounds in commercial IFs. According to the manufacturers' instructions, once opened IFs should be used within a month. Generally, they are consumed before this time. However, when IFs are used for complementary feeds, the product could be stored longer. Therefore it would be of interest to study the evolution of volatiles not only during the one-month's life once opened, but also after this time, extending the analysis, for example, until 70 days after opening, a period greater than double the established time for formula consumption.

Here we measured and analysed the quantity of propanal, pentanal and hexanal in several brands of milk-based IF, as potential indicators of lipid oxidation and consequently formula decomposition. For this purpose we used SHS-GC, a simple and sensitive method developed in our laboratory (Romeu-Nadal et al., 2004). In addition, we evaluated oxidative stability of IFs by examining the evolution of these volatiles and the fatty acid profiles during the 70 days after package opening. It is hypothesised that oxidative stability decreases quickly once packets are opened, as a result of product exposure to the action of oxygen and light, and that IFs with major contents of longchain (LC-PUFAs) generate more volatiles, due to their higher susceptibility to oxidation. Correlations between fatty acid losses and volatiles increase were measured.

2. Materials and methods

2.1. Samples

Twenty branded milk-based powdered IFs were purchased from several markets. Table 1 indicates the general composition of the studied formulae, as stated on the product label.

2.2. Storage

All IFs were opened on the same day; approximately in the 5–9 month of their shelf-lives. In addition, IFs were opened three times every day thereafter; each time the powder was stirred in the original packet to maintain uniform exposure to environment and two scoops of powder were discarded, thereby simulating normal storage and preparation. We kept the IFs at room temperature (25 °C: min 23 °C, max 25.5 °C), and the contents were analysed at 0, 15, 30, 50 and 70 days. The volatile compound content was determined on-line. We placed aliquots of approximately 15 g