Food Additives & Contaminants: Part A, 2014
Vol. 31, No. 8, 1385–1392, http://dx.doi.org/10.1080/19440049.2014.926400

Determination of 3-monochloropropane-1,2-diol fatty acid esters in Brazilian vegetable oils and fats by an in-house validated method

A.P. Arisseto*, P.F.C. Marcolino and E. Vicente

Food Science and Quality Center (CCQA), Institute of Food Technology (ITAL), Campinas, Brazil

(*Received 12 February 2014; accepted 15 May 2014*)

An in-house validated GC-MS method preceded by acid-catalysed methanolysis was applied to 97 samples of vegetable oils and fats marketed in Brazil. The levels of the compounds ranged from not detected (limit of detection = 0.05 mg kg^{-1}) to 5.09 mg kg^{-1}, and the highest concentrations were observed in samples containing olive pomace oil and in products used for industrial applications, such as palm oil and its fractions (olein and stearin). The content of diesters and monoesters was also investigated by employing solid-phase extraction on silica cartridges, indicating that the majority of the compounds were present as diesters. This study provides the first occurrence data on these contaminants in Brazil and the results are comparable with those reported in other countries.

Keywords: contaminants; 3-MCPD; oil refining; deodorisation

Introduction

3-Monochloropropane-1,2-diol (3-MCPD) is a well-known chemical contaminant belonging to the group of chloropropanols that can be found in processed foods and food ingredients both in free and bound form (Velíšek et al. 1980; Svejkovská et al. 2004). The latter correspond to fatty acid esters of 3-MCPD, which include different compounds, such as monoesters and diesters, depending on the number of esterified hydroxyl groups and the type of fatty acid present in the molecule (Seefelder et al. 2011).

Studies have shown that 3-MCPD esters may be present at concentrations significantly higher than the levels found for the free form, especially in edible oils and fats (Svejkovská et al. 2004; Zelinková et al. 2006). These findings raised an immediate concern in terms of public health due to the possibility of these compounds undergoing hydrolysis by enzymes in the human gut and representing an additional source of exposure to 3-MCPD, previously not considered (BfR 2007; European Food Safety Authority 2008; International Life Sciences Institute 2011). *In vitro* studies have already demonstrated the potential of 3-MCPD monoesters to undergo hydrolysis by lipases (Seefelder et al. 2008; Buhrke et al. 2011) and, more recently, experiments conducted with rodents indicated both the hydrolysis of diesters *in vivo* and the high bioavailability of 3-MCPD from these compounds after oral administration (Abraham et al. 2013). Free 3-MCPD has been associated with nephrotoxicity and ability to affect male fertility (Food and Agriculture Organization/World Health Organization 2001, 2007). In addition, this contaminant is classified as a possible human carcinogen (group 2B) by the International Agency for Research on Cancer (2012) in view of its potential to induce cancer in experiments with animals.

According to the German Federal Institute for Risk Assessment (BfR 2007), preliminary exposure estimates assuming complete hydrolysis of these esters during the digestion showed that the intake of specific population groups to free 3-MCPD could exceed its provisional maximum tolerable daily intake (PMTDI) of 2 µg kg^{-1} body weight (bw) established by the Food and Agriculture Organization/World Health Organization (2001, 2007), suggesting a potential risk to health. A more detailed exposure assessment recently conducted by European Food Safety Authority (2013) showed similar conclusions, indicating higher intakes for children and elderly groups. For these reasons, the contamination of foods with 3-MCPD esters has been considered a priority food safety issue.

In vegetable oils and fats, high concentrations of 3-MCPD esters have been frequently reported in palm oil (*Elaeis guineensis* Jacq.) and derived products for which levels up to 10 mg kg^{-1} have already been observed (Kuhlmann 2011). According to some authors, the compounds are formed from triglycerides and species of organic and inorganic chlorine resulting from endogenous metabolism of the plant and environmental contamination (Nagy et al. 2011; Destaillats et al. 2012). The formation occurs mainly during the deodorisation step of the refining process in which temperatures above 200°C are used (Franke et al. 2009; Hrncirik & Van Duijn 2011). For unrefined oils, concentrations below 0.4 mg kg^{-1} have been reported (Zelinková et al. 2006).

---

*Corresponding author. Email: adriana.arisseto@gmail.com

The proposed analytical approaches for determining 3-MCPD esters involve both indirect analysis, in which the total concentration of the compounds is measured as free 3-MCPD obtained after a hydrolysis/methanolysis procedure, and direct analysis, in which the different species of 3-MCPD esters are individually identified. Indirect methods have shown good application for routine purposes due to the need of a reduced number of analytical standards, but do not provide information about individual species unless a previous separation of the compounds is carried out. Most procedures described in the literature employ acid or alkaline-catalysed methanolysis to release 3-MCPD from the esters (Crews et al. 2013). However, the choice of the procedure must consider the presence of glycidyl esters in the samples, which can be hydrolysed to glycidol under alkaline conditions, overestimating the results as a consequence of 3-MCPD formation in the presence of chloride during the analysis (Weißhaar & Perz 2010). Recently, a collaborative study has validated three indirect methods for characterising 3-MCPD esters in oils and fats, which were adopted as AOCS Official Methods (American Oil Chemists' Society 2013).

The questions about the reliability of indirect methods as well as the limited availability of reference materials and commercial standards required for direct methods, which has improved only in the last few years, could possibly be some factors responsible for the lack of large-scale surveys concerning the occurrence of 3-MCPD esters (Crews et al. 2013). Although an extensive collection of data on the levels of 3-MCPD esters was recently reported in the United States (MacMahon et al. 2013) and China (Chung et al. 2013), many published results have still been derived from method testing experiments and studies of formation, especially in palm oil (Crews et al. 2013). In view of these considerations, the objective of this study was to provide a comprehensive database on the levels of 3-MCPD esters in vegetable oils and fats marketed in Brazil which is, to our knowledge, the first information about the occurrence of these contaminants in Brazilian products.

Materials and methods

Chemicals and standards

The following reagents and solvents were used in the analysis: tetrahydrofuran (THF, analytical grade, Sigma-Aldrich Corp., Steinheim, Germany); acid phenylboronic (PBA, 97% purity, Sigma-Aldrich); methanol (HPLC grade, Tedia Company Inc., Fairfield, OH, USA); hexane, acetone, sulfuric acid, sodium bicarbonate and ammonium sulfate (analytical grade, Labsynth, Diadema, SP, Brazil); diethyl ether (HPLC grade, Vetec, Duque de Caxias, RJ, Brazil); ethyl acetate (HPLC grade, JT Baker, Phillipsburg, NJ, USA); and dichloromethane (HPLC grade, Carlo Erba, Rodano, Italy). Water was purified by reverse osmosis (Gehaka, São Paulo, SP, Brazil).

3-MCPD-1,2-dipalmitoyl ester (PP-3-MCPD), 3-MCPD-1,2-dipalmitoyl-d_5 ester (PP-3-MCPD-d_5), 3-MCPD-1-oleoyl ester (1-O-3-MCPD) e 3-MCPD-1-oleoyl-d_5 ester (1-O-3-MCPD-d_5) were purchased from Toronto Research Chemicals (North York, ON, Canada). The stock solutions were prepared at a concentration of 0.5 mg ml^{-1} by dissolving the standards in tetrahydrofuran.

Samples

A total of 97 samples of vegetable oils and fats were analysed in relation to 3-MCPD esters. Sampling was made by considering previous data reported by other countries and included products destined for household consumption as well as used in industrial applications. Samples of household consumption, including different brands and different lots of each brand whenever available, were purchased at supermarkets from the city of Campinas, SP. Industrial products were kindly supplied by two local oil manufacturers. A certified reference material (CRM) of palm oil (T2634QC) produced by FAPAS (Food Analysis Performance Assessment Scheme) was used as analytical quality control.

Determination of 3-MCPD esters

3-MCPD esters were determined according to Zelinková et al. (2006) and Hrncirik et al. (2011), with some modifications mainly concerning the salt used for salting-out of fatty acid methyl esters (FAMEs). The sample (100 mg) was weighed in a screw cap tube and dissolved in 1 ml of PP-3-MCPD-d_5 0.5 µg ml^{-1} (prepared in THF). After addition of 1.8 ml of sulfuric acid in methanol (1.8%, v/v), the tube was sealed and incubated in a water bath at 40°C for 16 h for transesterification and release of 3-MCPD bound to fatty acids. The reaction was stopped by adding 0.5 ml of a saturated aqueous solution of sodium bicarbonate and the organic solvents were evaporated under a steam of N_2. FAMEs were removed by adding 2 ml of ammonium sulfate 20% followed by liquid–liquid extraction with hexane (2 × 2 ml). An aliquot of 250 µl of the derivatising solution (1 g of PBA dissolved in 4 ml of acetone–water, 19:1, v/v) was added to the aqueous extract. The tube was sealed, shaken for 15 s on a vortex mixer and heated in a water bath at 90°C for 40 min. After cooling at RT, 2 ml of hexane were added and the tube was vortexed for 30 s to extract the derivatised 3-MCPD. The supernatant (hexane) was transferred to a vial, stored in the freezer for at least 4 h and filtered through a cotton bed before injection into the chromatographic system.

Determination of 3-MCPD diesters and monoesters

3-MCPD diesters and monoesters were determined according to Seefelder et al. (2008) using SPE, with some modifications. For that, the sample (100 mg) was weighed into a gas chromatography vial and diluted with 50 µl of hexane. After addition of 50 µl of PP-3-MCPD-d_5 and 50 µl of 1-O-3-MCPD-d_5, both prepared in hexane at a concentration of 10 µg ml^{-1}, the sample was applied onto an SPE silica cartridge HF Mega BE-SI 1 g/6 ml (Agilent Technologies, Palo Alto, CA, USA), and preconditioned with 4 ml of hexane. An aliquot of 4 ml of hexane was passed through the cartridge and discarded. 3-MCPD diesters were then eluted with 8 ml of a mixture of hexane/dichloromethane/diethyl ether (89:10:1). An aliquot of 2 ml of a mixture of hexane/ethyl acetate (85:15) solution was passed through the cartridge and discarded. 3-MCPD monoesters were finally eluted with 15 ml of hexane/ethyl acetate (85:15). (The SPE was performed without a vacuum pump at a flow rate of approximately 0.7 ml min^{-1}). The extracts resulting from the elution of diesters and monoesters were collected separately in 10 ml screw cap tubes and evaporated under a steam of N_2. The residue was dissolved in 1 ml of THF. Transesterification and derivatisation were performed as previously described. This procedure was applied only to samples for which the total amount of 3-MCPD esters was higher than 0.20 mg kg^{-1}.

Chromatographic analysis

The experiments were conducted on an HP 7890A gas chromatograph coupled to a MSD 5975C mass spectrometer (Agilent Technologies). An aliquot of 1 µl of the extract was introduced into the injector operating at 180°C in splitless mode. The separation was carried out on a capillary column VF-1ms 30 m × 0.25 mm (0.25 µm) (Agilent Technologies) using helium as the carrier gas at a flow rate of 1.2 ml min^{-1}. The following temperature programme was used in the oven: 60°C (held for 1 min), 6°C min^{-1} to 190°C, 20°C min^{-1} to 280°C (held for 30 min). Detection was performed by SIM after positive electron impact ionisation (70 eV). The following ions were monitored: *m/z* 147, 91 and 196 for 3-MCPD and *m/z* 150, 93 and 201 for the internal standard 3-MCPD-d_5.

Method validation

The methods were in-house validated in relation to linearity, selectivity, LOD, LOQ, trueness (analysis of CRM and recovery) and precision (repeatability and within-laboratory reproducibility) according to the guidelines laid down by the National Institute of Metrology, Quality and Technology (Instituto Nacional de Metrologia, Normalização e Qualidade Industrial 2010). Linearity was evaluated using eight calibration points. Selectivity was determined by a comparison between curves set on standard solutions and on matrix by applying the *F*-test and *t*-test. LOD and LOQ were calculated as three- and six-fold standard deviation of six independent sample blanks measured once each. Recovery, repeatability and within-laboratory reproducibility were evaluated by spiking a blank sample with PP-3-MCPD (and 1-O-3-MCPD in the case of SPE experiments) at 0.1, 0.4 and 2 mg kg^{-1} (six replicates for each concentration level). A sample of extra virgin olive oil, for which the presence of 3-MCPD esters was not detected, was used as a blank sample.

Results and discussion

Method validation

The method used for the determination of 3-MCPD esters, which was based on acid-catalysed methanolysis using ammonium sulfate for salting-out of FAMEs, showed excellent linearity (0–8.6 mg kg^{-1}; $r^2 = 0.999$) and non-significant matrix effects ($F_{calc} = 1.11 < F_{tab} = 3.79$; $t_{calc} = 0.13 < t_{tab} = 2.14$). LOD and LOQ were set at 0.05 and 0.10 mg kg^{-1}, respectively. The deviation between the experimentally determined concentration and the certified value of the CRM ranged from –0.9% to 8.4% (six replicates in two different days). Recovery and precision were considered satisfactory (Table 1).

In order to compensate for the limitation of indirect methods concerning the lack of information about individual species of 3-MCPD esters, a procedure employed for the separation of diesters and monoesters using SPE before the transesterification step was also validated. The separation of the compounds was first controlled by monitoring the separation of two isotopically labelled standards (PP-3-MCPD-d_5 and 1-O-3-MCPD-d_5) in the presence of oil matrix (extra virgin olive oil and refined soybean oil). The eluates were collected in different fractions and analysed for the occurrence of 3-MCPD-d_5 after acid transesterification. Additional experiments showed no significant amounts of diesters in the intermediate fraction collected between the elution of diesters and monoesters

Table 1. Recovery and precision for 3-MCPD esters by acid-catalysed methanolysis.

Spike level (mg kg^{-1})	R (%)	CV_r (%)	CV_R (%)
0.1	110	8.4	6.1
0.4	101	4.4	3.9
2.0	105	4.4	4.0

Note: R, recovery (12 replicates for each spike level); CV_r, coefficient of variation under repeatability conditions (same day, six replicates for each spike level); and CV_R, coefficient of variation under within-laboratory reproducibility conditions (same laboratory, 2 different days, 12 replicates for each spike level).

and no additional monoesters eluted when the solvent volume in the final elution was doubled or polar eluents were used.

The method showed good linearity in the range of 0–4 mg kg^{-1} (r^2 = 0.999) and no matrix effect. LOD and LOQ were calculated as 0.1 and 0.2 mg kg^{-1}, respectively, for both PP-3-MCPD and 1-O-3-MCPD. Mean recoveries varied from 74% to 98% and coefficients of variation ranged from 6.9% to 11.5% for repeatability and from 6.8% to 16.2% for within-laboratory reproducibility (Table 2), showing the reliability of the procedure.

In relation to the quantitative approach, Seefelder et al. (2008) suggested determining the amounts of 3-MCPD monoesters, and then calculating the amounts of 3-MCPD diesters by subtracting the amounts of 3-MCPD monoesters from the total amount of 3-MCPD esters. This was proposed since the authors observed that the PP-3-MCPD-d$_5$ solution was only stable over a limited period. However, in contrast to these observations, we noted a good stability of the PP-3-MCPD-d$_5$ solution and demonstrated that the indirect calculation of 3-MCPD monoesters could also be possible considering only the fraction resulting from the elution of 3-MCPD diesters and the total amount of the compounds. This could be more advantageous taking into account that the majority of 3-MCPD esters correspond to diester forms and that a higher incidence of non quantifiable results could be expected for monoesters.

3-MCPD esters in vegetable oils and fats

Table 3 shows the levels of 3-MCPD esters determined in samples of edible oils and fats destined to household consumption. The concentrations ranged from not detected to 5.09 mg kg^{-1} (52 samples with levels above the LOQ). Most of the samples (73%) presented levels below 0.30 mg kg^{-1}, especially sunflower and canola oils. *Dendê*, which is the unrefined palm oil used for culinary preparations in Brazil, showed concentrations up to 0.33 mg kg^{-1}, suggesting that some products may contain a mixture of refined and unrefined oils or that the oil extraction conditions can led to the formation of 3-MCPD esters. Slightly higher values were found in hydrogenated vegetable fat (0.29–0.45 mg kg^{-1}) and sesame oil (0.48–0.58 mg kg^{-1}). According to MacMahon et al. (2013), 3-MCPD esters can be formed during the toasting of sesame seeds, contributing to the contamination of the unrefined oil.

Table 2. Recovery and precision for 3-MCPD diesters and monoesters.

Analyte	Spike level (mg kg^{-1})	R (%)	CV$_r$ (%)	CV$_R$ (%)
PP-3-MCPD	0.2	77	11.5	13.3
	1.0	89	9.7	9.9
	4.0	74	7.0	6.8
1-O-3-MCPD	0.2	98	10.8	16.2
	1.0	90	7.3	14.4
	4.0	83	6.9	12.1

Notes: R, recovery (12 replicates for each spike level); CV$_r$, coefficient of variation under repeatability conditions (same day, six replicates for each spike level); and CV$_R$, coefficient of variation under within-laboratory reproducibility conditions (same laboratory, 2 different days, 12 replicates for each spike level). PP-3-MCPD = 3-MCPD-1,2-dipalmitoyl ester; and 1-O-3-MCPD = 3-MCPD-1-oleoyl ester.

Concentrations above 1 mg kg^{-1} were reported in two samples of soybean oil, two samples of maize oil and in three samples of olive oil. The highest amounts (5.09 and 1.46 mg kg^{-1}) were observed in samples of olive oil that contained pomace oil. High levels of 3-MCPD esters in pomace oil were already reported by other authors, which could explain the concentrations observed in these products (Zelinková et al. 2006; Karšulínová et al. 2007). However, a sample of olive oil that was labelled as extra virgin showed a concentration of 1.29 mg kg^{-1}. As 3-MCPD esters should not be present at significant amounts in extra virgin olive oil (because it is unrefined), this level of contamination could indicate the presence of refined olive oil or pomace oil that was not declared on the label.

Considering individual lots, slight differences on the concentration of 3-MCPD esters were observed for most of the samples, with exception of a particular brand of soybean oil (A) and extra virgin olive oil (B), for which a remarkable variation was verified between two analysed lots. For some types of oils, such as soybean and maize, large differences were also observed among different brands. It is difficult to explain the cause of these variations, since the exact mechanism of formation and main precursors involved in the reaction are not completely understood. However, these data could suggest a potential for mitigation of 3-MCPD esters in these products.

Table 3 also shows the % of diesters found in 33 samples of oils for which the total amount of 3-MCPD esters was higher than 0.20 mg kg^{-1}. The levels of the compounds varied from <0.20 to 4.07 mg kg^{-1} and represented from 69% to 94% of the total concentration of 3-MCPD esters, considering 17 positive samples (above the LOQ). The lowest concentration of diesters (69%) was observed in a sample of sesame oil. These results confirm the higher occurrence of diesters in oils and fats, as already verified by other authors (Seefelder et al. 2008; MacMahon et al. 2013; Yamazaki et al. 2013).

The concentrations of 3-MCPD esters in oils and fats used for industrial applications are reported in Table 4. The levels of the compounds varied from 0.10 to 3.87 mg kg^{-1} and all samples presented quantifiable results. Some variation among different brands

Table 3. Levels of 3-MCPD esters in samples of vegetable oils and fats destined to household consumption (mg kg^{-1}, expressed as free 3-MCPD).

		3-MCPD esters ± variation (% of diesters)	
Sample	Origin	Lot 1	Lot 2
Soybean (A)	Brazil	1.19 ± 0.02 (80)	0.19 ± 0.01
Soybean (B)	Brazil	n.d.	<0.10
Soybean (C)	Brazil	<0.10	0.16 ± 0.04
Soybean (D)	Brazil	0.37 ± 0.04 (86)	0.34 ± 0.01 (80)
Soybean (E)	Brazil	1.11 ± 0.13 (94)	
Soybean (F)	Brazil	0.23 ± 0.00 (–)	0.21 ± 0.05 (–)
Maize (A)	Brazil	0.12 ± 0.01	<0.10
Maize (B)	Brazil	<0.10	
Maize (C)	Brazil	n.d.	n.d.
Maize (D)	Brazil	0.20 ± 0.00 (–)	
Maize (E)	Brazil	<0.10	<0.10
Maize (F)	Brazil	1.12 ± 0.05 (93)	1.04 ± 0.01 (90)
Sunflower (A)	Brazil	0.16 ± 0.01	0.14 ± 0.02
Sunflower (B)	Brazil	0.15 ± 0.02	0.13 ± 0.01
Sunflower (C)	Brazil	0.20 ± 0.02 (–)	0.10 ± 0.00
Sunflower (D)	Brazil	0.21 ± 0.03 (–)	0.22 ± 0.00 (–)
Sunflower (E)	Brazil	0.25 ± 0.01 (–)	0.27 ± 0.06 (–)
Sunflower (F)	Brazil	0.25 ± 0.07 (–)	
Canola (A)	Brazil	0.16 ± 0.02	0.13 ± 0.00
Canola (B)	Brazil	0.10 ± 0.02	<0.10
Canola (C)	Brazil	0.11 ± 0.02	0.30 ± 0.04 (75)
Canola (D)	Brazil	<0.10	0.14 ± 0.03
Canola (E)	Brazil	0.14 ± 0.00	0.25 ± 0.07 (–)
Canola (F)	Brazil	0.14 ± 0.03	0.24 ± 0.03 (–)
Canola (G)	Brazil	0.23 ± 0.03 (–)	
Maize, sunflower, canola (A)	Brazil	<0.10	0.12 ± 0.02
Maize, sunflower, canola (B)	Brazil	0.39 ± 0.02 (–)	
Olive extra virgin (A)	Spain	n.d.	n.d.
Olive extra virgin (B)	Portugal	1.29 ± 0.01 (72)	0.19 ± 0.03
Olive (virgin + refined) (A)	Spain	0.33 ± 0.08 (91)	0.14 ± 0.03
Olive + pomace (A)	Spain	1.46 ± 0.03 (81)	
Olive + pomace (B)	Portugal	5.09 ± 0.02 (80)	
Dendê (A)	Brazil	0.32 ± 0.02 (74)	0.25 ± 0.01 (–)
Dendê (B)	Brazil	0.30 ± 0.05 (–)	0.33 ± 0.02 (–)
Dendê (C)	Brazil	n.d.	
Peanut (A)	Brazil	0.13 ± 0.00	0.29 ± 0.03 (83)
Sesame (A)	Brazil	0.48 ± 0.00 (82)	0.58 ± 0.05 (69)
Hydrogenated vegetable fat (A)	Brazil	0.45 ± 0.08 (73)	0.29 ± 0.06 (74)

Notes: Number of samples = 67 (analysed in duplicate). *Dendê* is unrefined palm oil used for culinary preparations in Brazil. Letters in parentheses indicate different brands among the same products (the same letters for different types of oils do not necessarily correspond to the same brand). n.d., Not detected (below the LOD = 0.05 mg kg^{-1}); (–) = percentage of diesters was not calculated (concentration of diesters was below the LOQ = 0.20 mg kg^{-1}). The sampling of different lots was made by considering the information provided on the packaging, which is defined according to specific criteria of each manufacturer.

and lots can also be noted. Concentrations below 1 mg kg^{-1} were verified in 40% of the samples, including palm kernel oil, hydrogenated fats (all samples derived from soybean oil) and mix of fats (composition not informed by the producer). The highest levels (above 1 mg kg^{-1}) were clearly observed in products obtained from the pulp of palm, which corresponds to palm oil and its fractions (olein and stearin). These results are comparable with other data available in the literature (Karšulínová et al. 2007; Kuhlmann 2011; MacMahon et al. 2013; Yamazaki et al. 2013).

The amount of diesters in 28 samples of industrial oils and fats for which the total amount of 3-MCPD esters was higher than 0.20 mg kg^{-1} ranged from 0.22 to 3.52 mg kg^{-1} (all samples above the LOQ). According to Table 4, diesters represented from 59% to 96% of the total concentration of 3-MCPD esters. The lowest percentages were observed in palm olein

Table 4. Levels of 3-MCPD esters in samples of vegetable oils and fats used for industrial applications (mg kg^{-1}, expressed as free 3-MCPD).

		3-MCPD esters ± variation (% of diesters)					
Sample	Origin	Lot 1	Lot 2	Lot 3	Lot 4	Lot 5	Lot 6
Palm oil (A)	n.i.	1.05 ± 0.03 (74)					
Palm oil (B)	Brazil	2.32 ± 0.02 (96)	2.23 ± 0.03 (87)	2.09 ± 0.02 (85)	2.95 ± 0.25 (83)		
Palm olein (A)	n.i.	1.30 ± 0.00 (68)					
Palm kernel oil (A)	n.i.	0.17 ± 0.05					
Palm fat (for general use) (A)	Brazil	3.31 ± 0.03 (80)	1.64 ± 0.01 (81)				
Palm fat (for frying) (A)	Brazil	2.20 ± 0.02 (79)	2.56 ± 0.03 (79)				
Palm fat (for pastry) (A)	Brazil	2.29 ± 0.05 (83)	2.31 ± 0.01 (88)	2.51 ± 0.02 (86)	2.60 ± 0.02 (93)		
Palm fat (for ice cream) (A)	Brazil	2.45 ± 0.08 (79)	1.47 ± 0.03 (93)				
Shortening (A)	Brazil	3.14 ± 0.02 (84)	3.87 ± 0.03 (91)				
Mix of fats (A)	n.i.	0.66 ± 0.04 (69)	0.58 ± 0.00 (78)	0.60 ± 0.01 (73)	0.40 ± 0.00 (69)	0.43 ± 0.02 (66)	0.43 ± 0.03 (64)
Hydrogenated fat (A)	n.i.	0.10 ± 0.01	0.37 ± 0.01 (59)	0.35 ± 0.00 (82)	0.57 ± 0.03 (84)	0.58 ± 0.03 (96)	

Notes: Number of samples = 30 (analysed in duplicate). Letters in parentheses indicate different producers for the same product (the same letters for different products do not necessarily correspond to the same producer). Palm fat and shortening correspond to a mixture of palm oil and palm stearin. Hydrogenated fat is derived from soybean oil. n.i., Not informed. The difference among lots is based on specific criteria of each manufacturer.

(68%), as also reported by MacMahon et al. (2013), as well as in the samples of mix of fats (64–78%) and in one sample of hydrogenated fat (59%).

Conclusions

The present study reported the results of a survey on 3-MCPD esters in 97 samples of vegetable oils and fats commercialised in Brazil. The highest concentrations were verified in samples containing olive pomace oil and in products obtained from the pulp of palm, such as palm oil and its fractions (olein and stearin), confirming previous data published in other countries. Most 3-MCPD esters were present as diesters, which is highly relevant from a toxicological point of view. To our knowledge, these data correspond to the first information about the occurrence of 3-MCPD esters in national products and will be useful for a preliminary exposure estimate of the Brazilian population to these contaminants. Due to the high levels found in oils and fats used for industrial applications, it is highly important to evaluate the contamination of fried foods and other commercial processed foods by 3-MCPD esters in the future.

Funding

This work was supported by the São Paulo Research Foundation (FAPESP) [grant numbers 2011/08936-0 and 2011/19043-6].

References

Abraham K, Appel KE, Berger-Preiss E, Apel E, Gerling S, Mielke H, Creutzenberg O, Lampen A. 2013. Relative oral bioavailability of 3-MCPD from 3-MCPD fatty acid esters in rats. Arch Toxicol. 87:649–659.

American Oil Chemists' Society. 2013. AOCS validates methods for MCPD ester analysis [Internet]. [cited 2014 May 7]. Available from: http://www.aocs.org/Methods/index.cfm?navItemNumber=584

Buhrke T, Weißhaar R, Lampen A. 2011. Absorption and metabolism of the food contaminant 3-chloro-1,2-propanediol (3-MCPD) and its fatty acid esters by human intestinal Caco-2 cells. Arch Toxicol. 85:1201–1208.

[BfR] Bundesinstitut für Risikobewertung. 2007. Frequently asked questions about 3-monochloropropane-1,2-diol (3-MCPD) [Internet]. [cited 2014 Feb 12]. Available from: http://www.bfr.bund.de/en/frequently_asked_questions_about_3_monochloropropane_1_2_diol__3_mcpd_-60844.html

Chung SWC, Benny TP, Chan HY, Chung YX, Ho YY. 2013. Occurrence of bound 3-monochloropropan-1,2-diol content in commonly consumed foods in Hong Kong analysed by enzymatic hydrolysis and GC-MS detection. Food Addit Contam: Part A. 30:1248–1254.

Crews C, Chiodini A, Granvogl M, Hamlet C, Hrnčiřík K, Kuhlmann J, Lampen A, Scholz G, Weißhaar R, Wenzl T, et al. 2013. Analytical approaches for MCPD esters and glycidyl esters in food and biological samples: a review and future perspectives. Food Addit Contam: Part A. 30:11–45.

Destaillats F, Craft BD, Sandoz L, Nagy K. 2012. Formation mechanisms of monochloropropanediol (MCPD) fatty acid diesters in refined palm (Elaeis guineensis) oil and related fractions. Food Addit Contam: Part A. 29:29–37.

European Food Safety Authority. 2008. Statement of the Scientific Panel on Contaminants in the Food Chain (CONTAM) on a request from the European Commission related to 3-MCPD esters [Internet]. [cited 2014 Feb 12]. Available from: http://www.efsa.europa.eu/en/efsajournal/doc/1048.pdf

European Food Safety Authority. 2013. Analysis of occurrence of 3-monochloropropane-1,2-diol (3-MCPD) in food in Europe in the years 2009–2011 and preliminary exposure assessment. EFSA Journal, 11, 3381 [Internet]. [cited 2014 Feb 12]. Available from: http://www.efsa.europa.eu/en/efsajournal/doc/3381.pdf

Food and Agriculture Organization/World Health Organization. 2001. Safety evaluation of certain food additives and contaminants. 3-chloro-1,2-propanediol. WHO Food Additives Series, 48.

Food and Agriculture Organization/World Health Organization. 2007. Safety evaluation of certain contaminants in foods. 3-chloro-1,2-propanediol. WHO Food Additives Series, 58.

Franke K, Strijowski U, Fleck G, Pudel F. 2009. Influence of chemical refining process and oil type on bound 3-chloro-1,2-propanediol contents in palm oil and rapeseed oil. LWT – Food Sci Technol. 42:1751–1754.

Hrncirik K, Van Duijn G. 2011. An initial study on the formation of 3-MCPD esters during oil refining. Eur J Lipid Sci Technol. 113:374–379.

Hrncirik K, Zelinkova Z, Ermacora A. 2011. Critical factors of indirect determination of 3-chloropropane-1,2-diol esters. Eur J Lipid Sci Technol. 113:361–367.

Instituto Nacional de Metrologia, Normalização e Qualidade Industrial. 2010. Orientação sobre validação de métodos de ensaios químicos DOQ-CGCRE-08. Revisão 03 [Internet]. [cited 2014 Feb 12]. Available from: http://www.inmetro.gov.br/sidoq/arquivos/cgcre/doq/doq-cgcre-8_03.pdf

International Agency for Research on Cancer. 2012. 3-Monochloro-1,2-propanediol. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, 101, 586 [Internet]. [cited 2014 Feb 12]. Available from: http://monographs.iarc.fr/ENG/Monographs/vol101/mono101-010.pdf

International Life Sciences Institute. 2011. MCPD and glycidyl esters in food products. Summary Report of a Workshop held in November 2011 in Brussels, Belgium, organised by the ILSI Europe Risk Assessment of Chemicals in Food Task Force and Process-related Compounds & Natural Toxins Task Force [Internet]. [cited 2014 Feb 12]. Available from: http://www.ilsi.org/Europe/Documents/MCPD%20Report%202012.pdf

Karšulínová L, Folprechtová B, Doležal M, Dostálová J, Velíšek J. 2007. Analysis of the lipid fractions of coffee creamers, cream aerosols, and bouillon cubes for their health risk associated constituents. Czech J Food Sci. 25:257–264.

Kuhlmann J. 2011. Determination of bound 2,3-epoxy-1-propanol (glycidol) and bound monochloropropanediol (MCPD) in refined oils. Eur J Lipid Sci Technol. 113:335–344.

MacMahon S, Begley TH, Diachenko GW. 2013. Occurrence of 3-MCPD and glycidyl esters in edible oils in the United States. Food Addit Contam: Part A. 30:2081–2092.

Nagy K, Sandoz L, Craft BD, Destaillats F. 2011. Mass-defect filtering of isotope signatures to reveal the source of chlorinated palm oil contaminants. Food Addit Contam: Part A. 28:1492–1500.

Seefelder W, Scholz G, Schilter B. 2011. Structural diversity of dietary fatty esters of chloropropanols and related substances. Eur J Lipid Sci Technol. 113:319–322.

Seefelder W, Varga N, Studer A, Williamson G, Scanlan FP, Stadler RH. 2008. Esters of 3-chloro-1,2-propanediol (3-MCPD) in vegetable oils: significance in the formation of 3-MCPD. Food Addit Contam: Part A. 25:391–400.

Svejkovská B, Novotny O, Divinová V, Réblová Z, Doležal M, Velíšek J. 2004. Esters of 3-chloropropane-1,2-diol in foodstuffs. Czech J Food Sci. 22:190–196.

Velisek J, Davidek J, Kubelka V, Janicek G, Svobodova Z, Simicova Z. 1980. New chlorine-containing organic compounds in protein hydrolysates. J Agric Food Chem. 28:1142–1144.

Weißhaar R, Perz R. 2010. Fatty acid esters of glycidol in refined fats and oils. Eur J Lipid Sci Technol. 112:158–165.

Yamazaki K, Ogiso M, Isagawa S, Urushiyama T, Ukena T, Kibune N. 2013. A new, direct analytical method using LC-MS/MS for fatty acid esters of 3-chloro-1,2-propanediol (3-MCPD esters) in edible oils. Food Addit Contam: Part A. 30:52–68.

Zelinková Z, Svejkovská B, Velíšek J, Doležal M. 2006. Fatty acid esters of 3-chloropropane-1,2-diol in edible oils. Food Addit Contam: Part A. 23:1290–1298.