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Investigation of the 3-Monochloropropane-1,2-Diol Levels in Edible Cooking Fats and Oils. A Case Study of the Kenyan Market

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Abstract Edible cooking oils which are solids or liquids at room temperature are either extracted or processed through chemical processes from various sources. During chemical preparation, contaminants such as 3-Monochloropropane-1,2-diol (3-MCPD) esters could result. 3-MCPD esters are formed during deodorization process as a result of high temperature and low moisture conditions in presence of chloride ion. This compound has been classified as carcinogenic and therefore of significant health concern. In Kenya, various refined oils are in the market for consumer use and their use is regulated by the standards or technical regulations which sets limits for various parameters. There is no data on the regulatory levels of 3-MCPD esters in the relevant edible oil standards in Kenya or east Africa to facilitate its control. This implies that there are chances that the consumers are exposed to unregulated levels of 3-MCPD despite the adverse health effects. This study sought to establish the levels of 3-MCPD esters in refined oils in the Kenyan market. The mean levels were compared with the minimum limit in the European Food Safety Authority (EFSA) of 0.8 µg/kg of the body weight. The study found that most of the refined oils in the country have significant levels of 3-MCPD esters when compared with the EFSA limits.

Keywords Edible cooking oils, 3-Monochloropropane-1,2-diol (3-MCPD) esters, Carcinogenic

1. Introduction

Most of the foods consumed by human beings contain fats and oils either processed or not. Apart from satiety, food has other symbolic meaning associated with dominion, affection, solace, security, stress reliever and honor [1]. Food contains nutrients which are classified as carbohydrates, dietary fibre, proteins, vitamins, water, minerals and lipids. Lipids can be solid called fats or liquid called oils. They can be of vegetable or animal origin and most of them are refined. They are triglyceride molecules which are esters made up of a glycerol backbone linked to three fatty acid molecules [2,3]. Oils are made up of large quantities of unsaturated fatty acids containing at least one double bond in the fatty acid chain. Dietary fats include *trans*-fats, monounsaturated, polyunsaturated and saturated fats. The structure of saturated fat is made up of single bond between carbon atoms throughout the fatty acid chain [4,5,6]. Polyunsaturated fats have multiples of double bonds between carbon atoms [7]. Refined edible oils are liquid at room temperature and when chilled turns to solid while fats are solids at room temperature [8,9].

Fats and oils are refined chemically or physically before use. The process of the chemical purification of refined fats and oils is aimed at improving the final consumer characteristics such as clear appearance, stability to oxidation, light color, taste and aroma [10]. Further, refining process is aimed at achieving the required regulatory quality and safety levels. Chemical refining involves processes such as degumming, neutralization, bleaching and deodorization. The degumming process is the removal of phospholipids while neutralization is the removal of free fatty acids by addition of hydroxide solution which results in the formation of soap as a by-product [11].

To remove unwanted odors and bittering agents from the crude oil to obtain a brand and odorless oil, deodorization step is carried out. This step involves distillation of the crude oils with steam at high conditions of temperatures of between 180-270℃, high vacuum and low pressure of 1.5-6.0 mbar to get rid of volatile compounds, free fatty acids and colors. In some cases, this process leads to the formation of 3-Monochloropropane-1,2-diol (3-MCPD) esters [12]. The 3-MCPD esters are believed to have been converted from triacylglycerol to cyclic acyloxonium in presence of chloride ions [13,14].

Several studies have shown that 3-MCPD esters are carcinogenic and therefore a potential health concern [15,16].

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The control Panel of European Food Safety Authority [16] investigated the effects of 3-MCPD on rats. Toxicity of the kidney was the significant effect [17]. Based on these results, a safe limit was set for human lifespan, maximum tolerable daily intake (MTDI) of 0.8 micrograms per kilogram of body weight daily (μg/kg body weight daily) [18]. The set limit for 3-MCPD by the joint Food Standards Australia and New Zealand (FSANZ) is 0.02 μg/kg body weight daily which is in line with EFSA standards. Joint committee of Expert on Food and Additives, FAO/WHO limit is 2 µg/kg body weight daily [19,20,21].

Kenyans consume diverse products of food containing edible cooking fats and oils. No data shows existence or levels of 3-MCPD in edible cooking fats and oils. Additionally, there are no published regulatory limits in the regional or Kenyan Standards to facilitate control.

2. Materials and Methods

Sampling and sample size

The fats and oils were sampled from various retail outlets in the Kenyan market. This study employed convenience method of sampling. A total of 57 brands of edible cooking fats and oils were recorded in Kenyan market during sampling period. Some of the samples were imported and others were locally manufactured. In this study, 30 samples of edible cooking fats and oils were sampled in triplicates. Analysis of the compound was done using American Oil Chemists society method [22].

Sample preparation

A portion of 250mg of edible fats and oils was weighed and put in 5*u*l centrifuge tubes and mixed with 1000*u*l of acetonitrile. The mixture was vortexed for 5minutes and centrifuged until a clear acetonitrile layer was obtained. 400*u*l of the acetonitrile layer was then transferred to a clean 2*u*l centrifuge tube and the solvent was removed under nitrogen stream at room temperature. The residue was reconstituted in 1*u*l of hexane and stored at -18℃ before analysis.

Isolation of 3-MCPD esters

The isolation of 3-MCPD esters was performed on a SunFire™C18 column (4.6 by 150 mm), 5*u*m particle, using a Waters 1525 HPLC system with Waters 2424 evaporative light scattering detector (ELSD). The column temperature was maintained at 30℃, the sample injection volume was 20*u*l and each sample was injected three times. The mobile phase was acetonitrile (solvent A) and isopropanol (solvent B). The isocratic elution was performed as: 51% A, 49% B. The flow rate was 1ul min-1and both of the eluents containing 3-MCPD esters were collected and combined. The solvent was removed under nitrogen stream at room temperature. The sample was then reconstituted in 100ul acetonitrile and stored at -18℃ before analysis.

Determination of 3-MCPDesters

The 3-MCPD was determined using High-Performance Liquid Chromatography (HPLC) fitted with Evaporative Light Scattering Detector (ELSD). The column temperature during analysis was maintained at 30℃ and the sample injection volume was 5*u*l. The mobile phase was composed of hexane (solvent A) and isopropanol (solvent B). The isocratic elution was performed as follows: 90% A, 10% B at a flow rate of 0.5ul min-1.

The identity of 3-MCPD esters was verified by Ultra-high performance Liquid Chromatography with Quadrupole Time-Of-Flight Mass Spectrometry (UPLC-Q-TOF MS). The contents of 3-MCPD esters in oil samples were determined by HPLC method after the above described procedures of sample preparation and isolation of 3-MCPD esters. The concentration of 3-MCPD esters was calculated as 3-MCPD di-esters (1,2-dioleoyl-3-chloropropanediol standard substance) and 3-MCPD monoesters (1-stearoyl-3-chloropropanediol standard substance). The quantitative analysis was based on the peak area of the retention time of 5.8 and 7.6 min, respectively. The calibration curve was constructed using the total 3-MCPD esters.

3. Results and Discussions

The relationship between the logarithm of the peak area and the logarithm of the corresponding concentration of the standard substances was determined. The working range for the calibration solutions was 0.00 to 50.0 mg/kg and the linearity (R^2) of 3-MCPD esters was 0.9981 as shown in Figure 1.

The limit of detection (LOD) and limit of quantification (LOQ) values were determined by injecting a series of diluted stock solutions containing very low concentrations of 3-MCPD to obtain signal to noise (S/N) ratio values [23]. It was found that the LOD and LOQ for 3-MCPD esters in oil matrix were 0.004 mg/kg and 0.009 mg/kg respectively.

The intermediate precision was evaluated by determining the relative standards deviation (RSD) of triplicate determinations of thirty spiked samples of the oil matrix in three different days. It was found to be 0.11 or 11% showing that the data was precise.

3-MCPD was detected in all the 30 samples. The concentrations of the 3-MCPD in most of the samples was higher than the consumption levels of 0.8 µg/kg body weight daily set by EFSA [16].

The concentration of 3-MCPD esters in mg/kg found in various edible cooking fats and oils purchased from local supermarkets and retail shops in Kenya are shown in table 1.

The European Scientific Committee on Food has labelled 3-MCPD as a non-genotoxic carcinogen and the Joint FAO/WHO Expert Committee on Food Additives (JECFA) has established a maximum tolerable daily intake (TDI) of 3-MCPD at 2μg/kg body weight [22]. A recent report by the European Food Safety Authority (EFSA) set a TDI limit of 0.8μg/kg body weight daily for3-MCPD [16]. A younger age group of humans, especially infants and toddlers, are low in body weight to tolerate the possible ingestion of high levels of 3-MCPD esters.

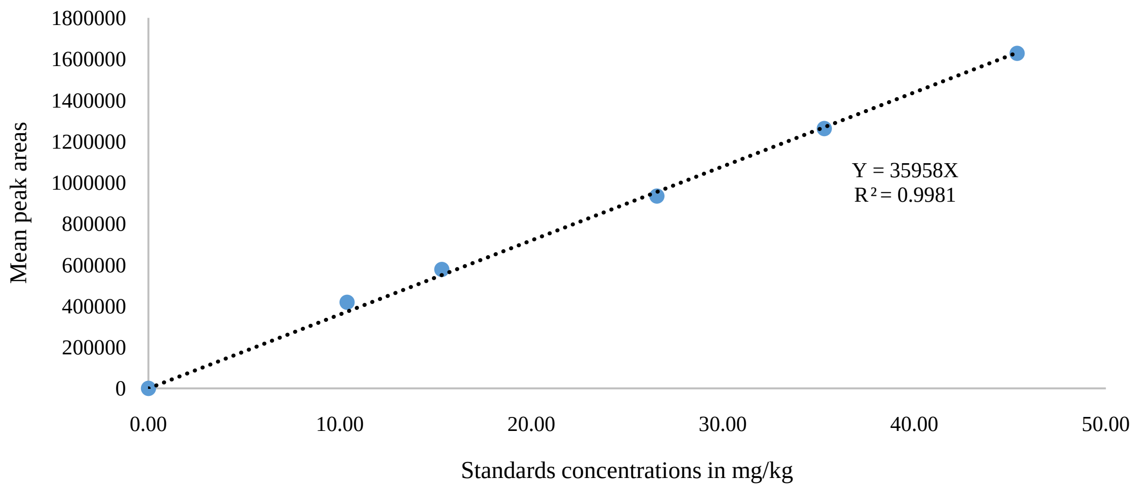

Figure 1. Calibration curve of the concentration of 3-chloropropane-1, 2- diol in n-hexane in mg/kg against mean peak areas

Table 1. Concentration of 3-MCPD in edible cooking fats and oils

SAMPLE No	SAMPLE CODE	TOTAL 3-MCPD (mg/kg)
1	BFO	0.72
2	UO	1.28
3	RO	1.80
4	PO	1.74
5	GFO	0.71
6	FFO	1.41
7	POO	1.1
8	SO	0.76
9	SG	0.77
10	TFO	0.70
11	PKO	2.31
12	SLO	4.26
13	SMEVO	1.75
14	AJEVO	0.95
15	KCO	0.79
16	KCF	0.99
17	SF	1.59
18	KF	1.52
19	CCF	2.40
20	MCF	1.78
21	KCF	0.20
22	FMF	1.88
23	ACF	1.31
24	MPCF	1.73
25	CCO	0.80
26	HFCO	2.00
27	RESCO	1.49
28	FFSCO	0.21
29	APVO	1.99
30	ECO	1.62

The presence of 3-Monochloropropane-1,2-diol (3-MCPD) is widely found in refined vegetable cooking fats and oils in its ester form as the food process contaminant. This contaminant occurs in a wide range of food stuffs. High-fat content products such as food emulsion, margarine and special fats contain a high level of 3-MCPD esters because they are directly derived from refined vegetable oils [24]. Consequently, the contaminant is found in foodstuff such as cereal products including bakery, cereal, biscuit, potatoes, snack foods, spreads and fried foods which is formed during domestic frying process.

3-MCPD esters have also been reported in non-thermal processed food such as cured fish and fresh dairy products. The possible formation of 3-MCPD esters is at relatively low temperatures of 40℃ when a system is comprised of vegetable oils, water, sodium chloride and lipase [15]. The report suggested that the formation of the 3-MCPD esters was via a lipase-catalyzed lipolysis of triacylglycerol (TAG) followed by nucleophilic attack of chloride anion. It is known that food with high fat content which has undergone thermal processing can be highly associated with the occurrence of 3-MCPD esters [25].

It was reported that baby formulas in the Brazilian market contain levels of 3-MCPD esters in baby foods to concentrations varying from 0.062 mg/kg to 0.588 mg/kg in the whole product [26]. It was deduced that the chance of containing 3-MCPD esters in infant formula was high because palm oil and palm olein are used in formulating the fatty acid profile for infant formula. Palm origin oils are generally high in the 3-MCPD esters [27].

4. Conclusions

This study reports high concentrations of 3-MCPD esters in refined edible cooking fats and oils in the Kenyan Market. The levels are above the regulatory limits set by the EFSA and other agencies. There are no regulatory limits for the Kenyan and East African regional market on the levels of consumption of 3-MCPD.

Declaration of the Conflict of Interest

The authors declare no conflict of interest.

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