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A REVIEW ON: PRODUCTION, USAGE, HEALTH EFFECT AND ANALYSIS OF MONO- and DIGLYCERIDES OF FATTY ACIDS

Hasan Hüseyin KARA*[a], Yasemin BOR[b]

[a]*Necmettin Erbakan University, Health Sciences Faculty, Nutrition and Dietetics Department, Konya, Turkey*
[b]*Afyon Kocatepe University, Graduate School of Natural and Applied Sciences, Food Engineering Department, Afyonkarahisar, Turkey*

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ABSTRACT

Mono- and diglycerides (M- and DG) are nonionic molecules containing both hydrophobic (with fatty acids) and hydrophilic (with -OH group) sides.While plant oils and animal fats are the natural sources for mono- and di-glycerides, they can be produced by either synthetically or enzymatically via direct esterification or transesterification processes. Because of stabilizing and conditioning properties, biodegradability, safe usage, and inertness in taste and odor, they are evaluated as emulsifying molecules mainly in food, cosmetic, pharmaceutical, textile and plastic industries. European Union (EU) defined mono- and di- glycerides of fatty acids as food additive and called as E471. The additives both improve functional properties and stabilize the foodstuff during production, storage and consumption. FDA and WHO indicate the additives as safe and no limitation on consumption while suitability of M- and DG for infants under the age of 12 weeks is not cleared yet. This study was prepared due to consumer concerns about the use of mono- and diglycerides of fatty acids as food additives. The aim of this study is the health concerns of consumers and also halal food concerns of Muslim consumers, regarding the use of mono- and diglycerides of fatty acids as food additives.

Keywords:
Mono- ve digliserit, gıda katkı Maddesi, gıda güvenliği, helal gıda

ÖZET

Mono- ve digliseritler (M- ve DG), hem hidrofobik (yağ asitleri ile) hem de hidrofilik (-OH grubuile) uçları içeren, iyonik olmayan moleküllerdir. Bitkisel yağlar ve hayvansal yağlar monogliseritler ve digliseritler için doğal kaynaklar olsa da, bunlar doğrudan esterifikasyon veya transesterifikasyon işlemleriyle sentetik veya enzimatik olarak üretilebilirler. Dengeleyici ve yumuşatıcı özellikleri, biyobozunurluk, güvenli kullanım ve tatta ve bazen de kokudaki kararsızlık nedeniyle, özellikle gıda, kozmetik, ilaç, tekstil ve plastik endüstrilerinde emülsifiye edici moleküller olarak değerlendirilirler. Avrupa Birliği (AB), yağ asitlerinin mono ve gliseritlerini gıda katkı maddesi olarak tanımlamıştır ve E471 olarak kodlamıştır.

***Corresponding author:** Assoc. Prof. Hasan Hüseyin KARA, E-mail: hasankara@erbakan.edu.tr* **Doi:**

Gıda katkı maddeleri hem fonksiyonel özellikleri geliştirmekte, hem de üretim, depolama ve tüketim sırasında gıda maddelerini stabilize etmektedir. FDA ve WHO, M- ve DG' nin güvenli olduğunu ve tüketimde sınırlama olmadığını belirtirken, M- ve DG 'in 12 haftalık bebeklerin tüketimi için uygunluğu henüz açıklığa kavuşturulamamıştır.

Bu çalışma, tüketicilerin yağ asitlerinin mono ve digliseritlerinin gıda katkı maddesi olarak kullanımı konusundaki endişeleri nedeniyle hazırlanmıştır. Bu çalışmanın amacı, yağ asitlerinin mono ve digliseritlerinin gıda katkı maddesi olarak kullanımıyla ilgili olarak tüketicilerin sağlık endişeleri ve ayrıca Müslüman tüketicilerin helal gıda endişelerinin değerlendirilmesidir.

Introduction

An emulsion is a mixture that consisting of at least two liquids that are usually immiscible. Many foods are formed by emulsions where small droplets of a liquid are dispersed within the other liquid or liquids. There are various types of emulsions based on the properties of continuous phase and dispersed phase. If the oil droplets are dispersed within a continuous aqueous phase, it is called "oil-in-water" (O/W)) type emulsion such as milk, mayonnaise, sauces, soups etc. On the other hand, if water droplets are dispersed in oil phase, they are in "water-in-oil" (W/O) type emulsions such as butter and margarine (Halmos, Mack and Gibson, 2019; Saltmarsh, 2015).

Basically, emulsifiers are substances to support blending oil and water homogenously by adsorbing the surface of droplets to prevent aggregation and flocculation (Halmos, Mack and Gibson, 2019; Dickinson, 2003; Mahungu, and Arzt, 2002). Mono- and diglycerides of fatty acids have amphiphilic specifications that is consisting of hydrophobic (with fatty acids) and hydrophilic (with -OH group) parts as in most of the emulsifiers (Singh and Mukhopadhyay, 2016; Foubert, Vanhoutte, and Dewettinck, 2004; Dickinson, 2003). They reduce interfacial tension during homogenization while are inhibiting aggregation to form stability of the emulsion (Halmos, Mack and Gibson, 2019).

Production

Fatty acids are the common parts of all lipids while lipids (oil and fats) are categorized by their composition, polarity and interaction ability. Glycerides, which are widely distributed form of fatty acids, are the corner stones to build dietary lipids with fatty acids (Pike and O'Keefe, 2017; Jannin, Rodier, and Musakhanian, 2014; Thompkinson, and Kharb, 2007; Fureby, Adlercreutz, and Mattiasson, 1996).

Some seed based oils are the source of mono- and di-glycerides naturally. Because of difficulties on isolation of these trace amounts of this molecules from the edible sources such as soy bean, olive oil, grapeseed oil and cottonseed oil, animal fat or other vegetable oils containing triglycerides are evaluated to perform chemical reactions to achieve mono- and di-glycerides. Triglycerides are transformed into mono- and di- glycerides by adding catalysts and heating, and then further processed such as distillation is required if it is used as food additive (CFR, 2018; Leonardis, Macciola, Niro, Nag, and Panfili, 2017; Fehily, 2016; Jannin, Rodier, and Musakhanian, 2014; Jannin, Rodier, and Musakhanian, 2014;

Krüger, Valerio, Balen, Ninow, Oliveira, Oliveira, and Corazza, 2010; De 2006; Foubert, Vanhoutte, and Dewettinck, 2004; Fureby, Adlercreutz, and Mattiasson, 1996; Kwon, Song, and Yoon, 1996).

Production of glycerides was first recorded in 1893 by esterification of fatty acids and glycerol. In the current industrial production, direct esterification and transesterification methods are two ways to manufacture mono- and di- glycerides as food additives. In the direct esterification process, glycerol and fatty acids derived from edible fats and oils by hydrolysis are reacted by stirring at 100-230ºC, mostly with a catalyst. In the transesterification process, natural or hydrogenated fats/oils obtained from a single or multiple sources to reach the desired fatty acid profile are reacted with glycerol. Mono-, di- and triglycerides mixture with unreacted glycerol are achieved at the end of glycolysis carried at 200-250ºC by an alkaline catalyst. At the end of both procedures, catalyst is neutralized, excess glycerol is removed by distillation and glycerides are purified by separation (Kantekin-Erdoğan, Ketenoglu and Tekin, 2019; EFSA 2017; Jannin, Rodier, and Musakhanian, 2014; Krüger, Valerio, Balen, Ninow, Oliveira, Oliveira, and Corazza, 2010; De 2006).

Food Applications

Developments on the techniques to produce foodstuff with extended shelf life, enhanced sensorial parameters and lower prices are driven by the changes of customer preferences and increased population around the world. Therefore, demand on food stability is increased where European Union (EU) defined 363 food additives as safe in EU Regulation 1129/20111 (EFSA, 2017; Saltmarsh, 2015). One of the common additives is mono- and diglycerides that can be derived from plant and animal sources in food industry. Mono- and diglycerides of fatty acids are defined as E471 in the list while monoglyceride esters such as acetic acid, lactic acid, citric acid, tartaric acid, diacetyl tartaric acid and mixed acetic and tartaric acid esters are listed as 472a, 472b, 472c, 472d, 472e and 472f, respectively (Halmos, Mack, and Gibson, 2019; Early, 2012). Dairy, meat, oily, bakery and cooked products, bakery products, chewing gums, beverages and salad dressings are the main applications where M- and DG are required (Saltmarsh, 2015; Early 2012; Foubert, Vanhoutte, and Dewettinck, 2004).

M- and DG are applied in foods consisting of oil based emulsions where a visible separation may be occurred over the time such as mayonnaise, margarine, skimmed milk concentrate and butter (Halmos, Mack and Gibson, 2019; Kantekin-Erdoğan, Ketenoglu and Tekin, 2019; La Fountaine, Gao and Williams III, 2016; Early 2012). In air in liquid emulsions, adding M- and DG to formula improves the structure. By this way, dispersion of air and fat with finer particle sizes in the products provides higher volume to bread, cakes, biscuits and baked products. Particularly, tartaric acid esters and of M- and DG improve gas bubble stability and gas retention which leads improved bread volume and softer texture in fermented products. On the other hand, effect on decelerating retrogradation of starch leads recrystallization of starch granules and separation of water from gelatinized matrix in bakery products as well as supporting protein and starch interaction. Moreover, M- and DG improve gluten protein network and inhibit leaving gases in

bread and cake dough to improve characteristics of the structure and sensorial parameters. By adding M- and DG to margarines and butters, effective emulsion and crystal modification can be produced. Furthermore, smoother texture and structure can be achieved on ice cream with improved air in liquid emulsion stability. By this way, freezing-melting stability is enhanced which retarding melting time of ice cream during consumption. Sticking during processes such as extruding of start based products can be inhibited by glycerides. Moreover, improved emulsion stability in processed meat products can be supported by M- and DG and their esters. By rearranging the structure of M- and DG, aroma and textural properties can be evaluated as substitution of high oil/fat content products (Kantekin-Erdoğan, Ketenoglu and Tekin, 2019; Early 2012; Foubert, Vanhoutte, and Dewettinck, 2004; Kayacıer and Singh, 2003).

Based on a data system worldwide, mono- and di- glycerides of fatty acids (E471) were added as an ingredient to and labeled on 33,090 different foods and beverages between 2012 and 2017. These products were detailed as desserts, ice cream, bakery products, baking powders and mixtures, pasta, margarine and butter while 7% of total food stuff was containing these additives (EFSA, 2017).

Dosage and Limitations

Today, depending on the application and desired requirements, various types of M- and DG are commercially available. Powder form provides ease to apply. 100-1000 micrometers of liquid mono- and diglycerides or distilled monoglyceride in a diameter can be applied by spraying. For bakery products, it is generally applied around 0.5-1%. Hydrates which are liquid above room temperature should be cooled with a heat exchanger and become crystallized. Recommended dose is around 0.5-1.25%. Distillation of M- and DG provides 90% purity and solid forms to be powder, flake or capsule. By this way, emulsifier can be melted inside oil for applications such as shortening, dressings and margarine. Shortening types can be also manufactured to produce emulsified products which might be in paste or pliable form. There is no clear limitation on dosing for products (Mahungu, and Arzt, 2002).

FDA and WHO indicate M- and DG additives as safe and no limitation for adults but for the infants under the age of 12 weeks should have some limits. So the limits of mono and di glycerides in infant formula and weaning foods were indicated as 4 g/L and 5 g/kg respectively by The Scientific Committee (SCF) (EFSA, 2017).

Recommended daily intake of mono- and di-glycerides of fatty acids (E471) should be around 0.8-3.5% of daily fat intake. Based on the reports on mono- and di-glycerides of fatty acids as food additive, no safety concern was indicated (CFR, 2018; EFSA, 2017).

Health Effects

Food fats present mostly triglycerides and have trace amount of mono and di-glycerides. Triglycerides are broken down to mono and di-glycerides in the gastrointestinal lumen by pancreatic lipase while mono- and di-glycerides absorbed by intestinal cells. No evidence was detected about harmful effect on cells or tissues. However, it is not applicable to infants under 12 weeks

(EFSA, 2017; Thompkinson, and Kharb, 2007). On the other hand, some scientists indicated that most of the tests were carried out on animals which may be differ from human digestion system. For instance, liver enlargement was reported on animals where the ingestion was around 15%. However, no histological changes were reported. By this way, it was stated that consuming mono- and diglycerides might have side effects to increase long chain saturated fatty acids in the body. Moreover, it is suggested that antagonistic and synergist effects with other additives in the body should be investigated (Halmos, Mack and Gibson, 2019).

Quantitative Analysis

Currently, general analytical methods are not effective to determine and differentiate M- and DG and natural ones from additives. Again, new and sophisticated techniques are necessary to determine their source if they are from animal or plant after the extraction of M- and DG from the food product. Silica gel column chromatography and thin layer chromatography (TLC) can be applied using with IUPAC method for bakery products. For dairy products, fat is extracted with organic solvent following an alkali digestion of proteins and TLC can be applied. High-performance thin-layer chromatography (HPTLC) can be applied to quantify di-glycerides of fatty acids in soya oil. High performance liquid chromatography (HPLC) is another method for measurement. M- and DG of fatty acids in edible oil can be measured by high temperature gas liquid chromatography. Gas chromatography-mass spectrometry (GC-MS) can be applied in edible oils in various methods. Characterization of M- and DG from fats can be carried out by bi dimensional gas chromatography coupled with time of flight mass spectrometry (GCXGC-TOF-MS). Another way to quantitative measurement is liquid chromatography/atmospheric-pressure chemical ionization mass spectrometry (LC-APCI-MS) in food matrices. For determination on molar-based concentrations, nuclear magnetic resonance (NMR) is another option (EFSA, 2017;Indrasti et. al. 2010).

Conclusion

Mono- and diglycerides of fatty acids are one of the crucial food additives which have wide application spectra. Their usage and side effects on health were indicated in some research. Although it is not allowed to use for infant foods under 12 weeks, there is no restrictions for consumption by adults that may be correlated with applied small quantities into the food. These additives (M- and DG) produced commercially mostly from some animal (mostly from lard) and plant (mostly soybean) sources which are the major sources for industrial production nowadays. The absence of origin details of mono- and diglycerdies and other food additives cause difficulties for customers to be sure and clear about the source of the product. In the line with these data and investigations, it is suggested to add and indicate origin details of food additives on label of the products.

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