

---

# **Processing Contaminants in Edible Oils**

**MCPD and Glycidyl Esters**

---

Editor

**Shaun MacMahon**



## **AOCS Mission Statement**

AOCS advances the science and technology of oils, fats, surfactants and related materials, enriching the lives of people everywhere.

## **AOCS Books and Special Publications Committee**

M. Mossoba, Chairperson, U.S. Food and Drug Administration, College Park, Maryland

W. Byrdwell, Vice Chair, USDA, ARS, BHNRC, FCMDL, Beltsville, Maryland

P. Dutta, Swedish University of Agricultural Sciences, Uppsala, Sweden

N.T. Dunford, Oklahoma State University, Oklahoma

D.G. Hayes, University of Tennessee, Knoxville, Tennessee

V. Huang, Yuanpei University of Science and Technology, Taiwan

L. Johnson, Iowa State University, Ames, Iowa

H. Knapp, Big Sky Medical Research, Billings, Montana

G. Knothe, USDA, ARS, NCAUR, Peoria, Illinois

D. Kodali, Global Agritech Inc., Minneapolis, Minnesota

G.R. List, USDA, NCAUR-Retired, Consulting, Peoria, Illinois

R. Moreau, USDA, ARS, ERRC, Wyndmoor, Pennsylvania

W. Warren Schmidt, Surfactant Consultant, Cincinnati, Ohio

P. White, Iowa State University, Ames, Iowa

N. Widlak, ADM Cocoa, Milwaukee, Wisconsin

R. Wilson, Oilseeds & Biosciences Consulting, Raleigh, North Carolina

Copyright © 2014 by AOCS Press, Urbana, IL 61802. All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means without written permission of the publisher.

ISBN 978-0-9888565-0-9 (print)

ISBN 978-1-6306703-1-3 (.epub)

ISBN 978-1-6306703-2-0 (.mobi)

## **Library of Congress Cataloging-in-Publication Data**

Processing contaminants in edible oils : MCPD and glycidyl esters / editor, Shaun MacMahon.  
pages cm.

ISBN 978-0-9888565-0-9 (hard cover : alk. paper) 1. Oils and fats, Edible—Deterioration.

I. MacMahon, Shaun, 1976— editor of compilation.

TX560.O3P76 2014

613.2'84—dc23

2014000115

Printed in the United States of America

18 17 16 15 14 5 4 3 2 1

The paper used in this book is acid-free, and falls within the guidelines established to ensure permanence and durability.

## Introduction

---

### Formation

To improve consumer acceptance, edible oils are industrially processed by removing or modifying components that can negatively impact appearance, taste, and shelf stability. However, undesirable chemical changes can take place during the refining process. Fatty acid esters of 3-chloro-1,2-propanediol (3-MCPD), 2-chloro-1,3-propanediol (2-MCPD), and glycidol are heat-induced contaminants that are not present in virgin unrefined oils, but they can be produced during high temperature deodorization (Hrnčířík and van Duijn, 2011; Matthäus et al., 2011; Pudiel et al., 2011). There is evidence that 3-MCPD esters are formed from iron chloride and/or natural organochlorines present in native oils (Destailats et al., 2012a, 2012b; Nagy et al., 2011). The predominant precursors and formation pathways for MCPD and glycidyl esters will be thoroughly reviewed in Chapter 1 of this text.

### Mitigation

The fact that MCPD esters begin forming at 200 °C makes mitigation difficult, as deodorizations are generally run at temperatures greater than 200 °C (Destailats, 2012a). Many factors contribute to the formation of MCPD and glycidyl esters. The growing conditions and harvesting of the palm fruit can have profound effects on an oil's capacity to form contaminants. The extraction, washing, and processing steps that take place prior to deodorization can influence the formation of these toxicants during deodorization, as can the specifics of the deodorization scheme. It is also possible to remove MCPD and glycidyl esters using appropriate adsorbents or enzymes. Chapter 2 of this text discusses the optimization of all of these steps to reduce and eliminate the presence of these contaminants in refined edible oils.

### Analysis

Processed edible oils are commonly consumed worldwide and used in the production of infant formula, which highlights the need for accurate analytical methodology for their detection. Indirect approaches, requiring ester hydrolysis followed by derivatization and analysis by GC-MS, were the first methods developed to detect these MCPD and glycidyl esters (Divinová et al., 2004; Weißhaar, 2008; Zelinková et al., 2006). It was these early methods that brought attention from industry and regulators to the presence of these contaminants in refined oils. However, the use of base-catalyzed hydrolyses was shown to be potentially unreliable, raising questions about

the trustworthiness of indirect methodology (Haines et al., 2011; Kaze et al., 2011). Recently, the quality of these methods has improved greatly, and the application of indirect methodology to the analysis of MCPD and glycidyl esters will be covered in Chapter 3.

Partly in response to the lack of dependability of early indirect methodology, direct methods were developed for glycidyl esters (GEs) and 3-MCPD esters, through which contaminants are analyzed intact as they occur in processed oils. However, there are a number of issues that must be considered in the application of direct methodology; Chapters 4 and 5 will review the analysis of intact esters.

### Toxicology

Free glycidol, 3-MCPD, and 2-MCPD all pose concerns from a food safety perspective. Glycidol is a genotoxic carcinogen that is probably carcinogenic to humans (IARC, 2000). According to the Federal Institute for Risk Assessment in Berlin, Germany (BfR), it should be kept at concentrations as low as are reasonably achievable in food (Bakhiya et al., 2011). Negative effects on kidneys and reproductive systems have been seen from 3-MCPD in toxicological studies (Cho et al., 2008), and it was classified by the European Scientific Committee on Food as a nongenotoxic threshold carcinogen (European Commission, 2001). There are toxicological concerns shown in limited studies related to 2-MCPD; one unpublished report showed that high doses affected striated muscles and the heart, as well as the kidneys and the liver in rats (Schilter et al., 2011).

Most toxicological work has been with the free forms of these contaminants, whereas research on the fatty acid esters that are formed in deodorized oils has begun more recently (Bakhiya et al., 2011; Buhrke et al., 2011; Schilter et al., 2011). Recent *in vivo* toxicological work has demonstrated that free 3-MCPD is liberated from the diester form in rats (Abraham et al., 2013) as is glycidol from glycidyl esters (Appel et al., 2013). Initial risk assessments conducted by the BfR have concluded that using a worst-case scenario, infants who are fed only commercial infant formulas could potentially ingest amounts of glycidol and 3-MCPD exceeding the Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives (JECFA) recommended maximum tolerable daily intake levels (Buhrke et al., 2011). The full results of all toxicological studies on these contaminants will be discussed in Chapters 6 and 7.

### Regulations

In response to the detection of 3-MCPD in hydrolyzed vegetable protein, soy sauce, and baked goods, many international organizations addressed the issue in those ma-

trices. The JECFA recommended a maximum tolerable daily intake for 3-MCPD of 2 µg/kg body weight per day (WHO, 2002). The European Commission established a maximum level of 20 µg/kg (ppb) for 3-MCPD in hydrolyzed vegetable protein and soy sauce (European Commission, 2006), which was also adopted by Food Standards Australia New Zealand (FSANZ) (FSANZ, 2003). The Codex Alimentarius adopted a maximum level of 400 µg/kg (ppb) in liquid condiments containing acid-hydrolyzed vegetable protein (excluding naturally fermented soy sauce) in 2008 (Codex Alimentarius, 2012). The U.S. Food and Drug Administration Compliance Policy Guide states that hydrolyzed vegetable protein that contains 3-MCPD at levels greater than 1 µg/g (ppm) is not generally recognized as safe (GRAS), and therefore is an unsafe food additive (U.S. Food and Drug Administration, 2008). Health Canada also set a maximum contaminant concentration of 1 µg/g (ppm) in Asian-style sauces (Health Canada, 2012). No specific regulations regarding MCPD or glycidyl ester concentrations in processed oils have been published at this time.

## References

- Abraham, K.; Appel, K. E.; Berger-Preiss, E.; Apel, E.; Gerling, S.; Mielke, H.; Creutzenberg, O.; Lampen, A. Relative Oral Bioavailability of 3-MCPD from 3-MCPD Fatty Acid Esters in Rats. *Arch. Toxicol.* **2013**, *87*, 649–659.
- Appel, K. E.; Abraham, K.; Berger-Preiss, E.; Hansen, T.; Apel, E.; Schuchardt, S.; Vogt, C.; Bakhiya, N.; Creutzenberg, O.; Lampen, A. Relative Oral Bioavailability of Glycidol from Glycidyl Fatty Acid Esters in Rats. *Arch. Toxicol.* **2013**, *87*, 1649–1659.
- Bakhiya, N.; Abraham, K.; Gürtler, R.; Appel, K. E.; Lampen, A. Toxicological Assessment of 3-Chloropropane-1,2-diol and Glycidol Fatty Acid Esters in Food. *Mol. Nutr. Food Res.* **2011**, *55*, 509–521.
- Buhrke, T.; Weißhaar, R.; Lampen, A. 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.* **2011**, *85*, 1201–1208.
- Cho, W. S.; Han, B. S.; Nam, K. T.; Park, K.; Choi, M.; Kim, S. H.; Jeong, J.; Jang, D. D. Carcinogenicity Study of 3-Monochloropropane-1,2-diol in Sprague-Dawley Rats. *Food Chem. Toxicol.* **2008**, *46*, 3172–3177.
- Codex Alimentarius. Codex General Standard for Contaminants and Toxins in Food and Feed, Codex Stan 193-1995; amended 2012. [www.codexalimentarius.org/download/standards/17/CXS\\_193e\\_2012.pdf](http://www.codexalimentarius.org/download/standards/17/CXS_193e_2012.pdf) (accessed December 17, 2013).
- Destailhats, F.; Craft, B. D.; Sandoz, L.; Nagy, K. Formation Mechanisms of Monochloropropanediol (MCPD) Fatty Acid Diesters in Refined Palm (*Elaeis guineensis*) Oil and Related Fractions. *Food Add. Contam. A.* **2012a**, *29*, 29–37.
- Destailhats, F.; Craft, B. D.; Dubois, M. L.; Nagy, K. Glycidyl Esters in Refined Palm (*Elaeis guineensis*) Oil and Related Fractions. Part I: Formation Mechanism. *Food Chem.* **2012b**, *131*, 1391–1398.

- Divinová, V.; Svejková, B.; Doležal, M.; Velíšek, J. Determination of Free and Bound 3-Chloropropane-1,2-diol by Gas Chromatography with Mass Spectrometric Detection Using Deuterated 3-Chloropropane-1,2-diol as Internal Standard. *Czech. J. Food Sci.* **2004**, *22*, 182–189.
- European Commission Health and Consumer Protection Directorate. Opinion of the Scientific Committee on Food on 3-Monochloro-propane-1,2-diol (3-MCPD), 2001. [http://ec.europa.eu/food/fs/sc/scf/out91\\_en.pdf](http://ec.europa.eu/food/fs/sc/scf/out91_en.pdf) (accessed December 17, 2013).
- European Commission Health and Consumer Protection Directorate. Commission Regulation (EC) No. 1881/2006 of 19 December 2006: Setting Maximum Levels for Certain Contaminants in Foodstuffs, 2006. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2006R1881:20100701:EN:PDF> (accessed December 17, 2013).
- FSANZ. *Chloropropanols in Food, An Analysis of the Public Health Risk*; Technical Report Series No. 15; Food Standards, Australia/New Zealand 2003. <http://www.foodstandards.gov.au/publications/Documents/Technical Report Chloropropanol Report 11 Sep 03.doc> (accessed December 17, 2013).
- Haines, T. D.; Adlaf, K. J.; Pierceall, R. M.; Lee, I.; Venkitasubramanian, P.; Collison, M. Direct Determination of MCPD Fatty Acid Esters and Glycidyl Fatty Acid Esters in Vegetable Oils by LC-TOF-MS. *J. Am. Chem. Soc.* **2011**, *88*, 1–14.
- Health Canada. Canadian Standards (Maximum Levels) for Various Chemical Contaminants in Foods, modified June 28, 2012. <http://www.hc-sc.gc.ca/fn-an/securit/chem-chim/contaminants-guidelines-directives-eng.php> (accessed December 17, 2013).
- Hrnčířik, K.; van Duijn, G. An Initial Study on the Formation of 3-MCPD Esters during Oil Refining. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 374–379.
- IARC (International Agency for Research on Cancer). *Some Industrial Chemicals*. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, Vol. 77; Lyon, France: International Agency for Research on Cancer, 2000; pp 469–486.
- Kaze, N.; Sato, H.; Yamamoto, H.; Watanabe, Y. Bidirectional Conversion between 3-Monochloro-1,2-propanediol and Glycidol in Course of the Procedure of DGF Standard Methods. *J. Am. Oil Chem. Soc.* **2011**, *88*, 1143–1151.
- Matthäus, B.; Pudel, F.; Fehling, P.; Vosmann, K. L.; Freudenstein, A. Strategies for the Reduction of 3-MCPD Esters and Related Compounds in Vegetable Oils. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 380–386.
- Nagy, K.; Sandoz, L.; Craft, B.; Destailats, F. Mass-Defect Filtering of Isotope Signatures to Reveal the Source of Chlorinated Palm Oil Contaminants. *Food Add. Contam.* **2011**, *28*, 1492–1500.
- Pudel, F.; Benecke, P.; Fehling, P.; Freudenstein, A.; Matthäus, B.; Schwaf, A. On the Necessity of Edible Oil Refining and Possible Sources of 3-MCPD and Glycidyl Esters. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 368–373.
- Schilter, B.; Scholz, G.; Seefelder, W. Fatty Acid Esters of Chloropropanols and Related Compounds: Toxicological Aspects. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 309–313.
- U.S. Food and Drug Administration. Guidance Levels for 3-MCPD (3-Chloro-1,2-propanediol) in Acid-Hydrolyzed Protein and Asian-Style Sauces. Compliance Policy Guide Section 500.500, March 14, 2008. <http://www.fda.gov/ICECI/ComplianceManuals/CompliancePolicyGuidanceManual/ucm074419.htm> (accessed December 17, 2013).

- Weißhaar, R. Determination of Total 3-Chloropropane-1,2-diol (3-MCPD) in Edible Oils by Cleavage of MCPD Esters with Sodium Methoxide. *Eur. J. Lipid Sci. Technol.* **2008**, *110*, 183–186.
- WHO. *Safety Evaluation of Certain Food Additives and Contaminants, 3-Chloro-1,2-propanediol*, WHO Food Additives Series 48, 2002. <http://www.inchem.org/documents/jecfa/jecmono/v48je18.htm> (accessed December 17, 2013).
- Zelinková, V.; Svejková, B.; Doležal, M.; Velíšek, J. Fatty Acid Esters of 3-Chloropropane-1,2-diol in edible oils. *Food Add. Contam.* **2006**, *23*, 1290–1298.