

THERMAL DEGRADATION OF
CANTHAXANTHIN IN A MODEL
SYSTEM UNDER TIME AND
TEMPERATURE CONDITIONS OF
VARIOUS FOOD PROCESSES

ROSHDY, TARIK HUSSEIN
DEGREE DATE: 1986

U·M·I Dissertation
Information Service

THERMAL DEGRADATION OF CANTHAXANTHIN IN A
MODEL SYSTEM UNDER TIME AND TEMPERATURE
CONDITIONS OF VARIOUS FOOD PROCESSES

By TARIK HUSSEIN ROSHDY

A dissertation submitted to the
Graduate School-New Brunswick
Rutgers, The State University of New Jersey,
in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy
Graduate Program in Food Science

Written under the direction of
Professor Henryk Daun
and approved by

Elizabeth F. ...
Ch. Tang 1to
Roy S. Marchand
[Signature]

New Brunswick, New Jersey

October 1986

© 1986

TARIK HUSSEIN ROSHDY

ALL RIGHTS RESERVED

This is an authorized facsimile, made from the microfilm master copy of the original dissertation or masters thesis published by UMI.

The bibliographic information for this thesis is contained in UMI's Dissertation Abstracts database, the only central source for accessing almost every doctoral dissertation accepted in North America since 1861.

U·M·I Dissertation Information Service

University Microfilms International
A Bell & Howell Information Company
300 N. Zeeb Road, Ann Arbor, Michigan 48106
800-521-0600 OR 313/761-4700

**Printed in 1988 by xerographic process
on acid-free paper**

Roshdy, Tarik Hussien

THERMAL DEGRADATION OF CANTHAXANTHIN IN A MODEL SYSTEM
UNDER TIME AND TEMPERATURE CONDITIONS OF VARIOUS FOOD
PROCESSES

Rutgers University The State U. of New Jersey (New Brunswick) PH.D. 1986

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

Copyright 1986

by

Roshdy, Tarik Hussien

All Rights Reserved

INFORMATION TO USERS

While the most advanced technology has been used to photograph and reproduce this manuscript, the quality of the reproduction is heavily dependent upon the quality of the material submitted. For example:

- Manuscript pages may have indistinct print. In such cases, the best available copy has been filmed.
- Manuscripts may not always be complete. In such cases, a note will indicate that it is not possible to obtain missing pages.
- Copyrighted material may have been removed from the manuscript. In such cases, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, and charts) are photographed by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is also filmed as one exposure and is available, for an additional charge, as a standard 35mm slide or as a 17"x 23" black and white photographic print.

Most photographs reproduce acceptably on positive microfilm or microfiche but lack the clarity on xerographic copies made from the microfilm. For an additional charge, 35mm slides of 6"x 9" black and white photographic prints are available for any photographs or illustrations that cannot be reproduced satisfactorily by xerography.

PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark ✓.

1. Glossy photographs or pages _____
2. Colored illustrations, paper or print _____
3. Photographs with dark background _____
4. Illustrations are poor copy _____
5. Pages with black marks, not original copy _____
6. Print shows through as there is text on both sides of page _____
7. Indistinct, broken or small print on several pages ✓
8. Print exceeds margin requirements _____
9. Tightly bound copy with print lost in spine _____
10. Computer printout pages with indistinct print _____
11. Page(s) _____ lacking when material received, and not available from school or author.
12. Page(s) _____ seem to be missing in numbering only as text follows.
13. Two pages numbered _____. Text follows.
14. Curling and wrinkled pages _____
15. Dissertation contains pages with print at a slant, filmed as received _____
16. Other _____

University
Microfilms
International

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

IN THE NAME OF GOD, MOST GRACIOUS, MOST MERCIFUL

ABSTRACT OF THE THESIS

Thermal Degradation of Canthaxanthin in a Model System Under Time and Temperature Conditions of Various Food Processes

By TARIK HUSSEIN ROSHDY, Ph.D.

Dissertation Director: Professor Henryk Daun

Carotenoids are one of the most important groups of natural pigments found in the plant and animal kingdoms. Canthaxanthin is an important oxygenated carotenoid. It occurs in many raw foods such as poultry, eggs, fish and crustaceans. It is also one of the approved food colorants. There is no published information available on thermal degradation products of canthaxanthin.

A model system has been developed to study chemical reactions involved in the heat treatment of canthaxanthin. Time and temperature conditions were selected to simulate deep fat frying, broiling, baking, roasting, drying, and boiling. Canthaxanthin was heated at 210°C, 175°C, and 100°C for 4, 2, 1 and 1/2 hours in glycerol.

Twenty-three compounds from the volatile thermal degradation products (TDP) of canthaxanthin were tentatively identified by gas chromatography and mass spectrometry as follows: Heptane; Methyl-cyclohexane; 2-Methyl-1,3,5-hexatriene; Methylbenzene(Toluene); 4-Methyl-3-penten-2-one; 1,2-Dimethylbenzene (O-xylene); 1,3-Di-methylbenzene(m-xylene); 3,4,4-Tri-methyl-2-cyclohexen-1-one; Methyl(1-Methylethenyl)benzene; 1-Ethenyl-3,5-dimethylbenzene; 1,4-Dimethyl-2-(1-methyl-ethenyl)benzene; 5-Methyl-2-(1-methylethyl)-2-cyclohexen-

1-one; 1,2-Di-hydro-6-methylnaphthalene; 1,2-Dihydro-2-methylnaphthalene; 1,3,5-Trimethyl-2-(1,2-propadienyl)benzene; (1-methylethylidene)cyclo-propylbenzene; 1,2-Di-hydro-2,5,8-trimethylnaphthalene; 2,6-di-methyl-naphthalene; 1,3,5-Trimethyl-2-(3-methyl-1,3-butadiene)-benzene; 1,2,3-Trihydro-4-keto-1,1,6-trimethylnaphthalene; 1,2-Dimethyl-4-(phenylmethyl)-benzene; 2-(1,1,5-Trimethyl-4-keto-cyclohex-1-enyl-1-toluene-1-ethene; 2,6-Dimethyl-9-(1,1,5-trimethyl-4-keto-1-cyclohexenyl)-1,3,5,7-octatetraene.

Five non-volatile compounds were tentatively identified from thermal decomposition products of canthaxanthin under conditions of our experiments using UV-visible, IR, and mass spectrometry techniques as follows: 3,7-Dimethyl-8-tolunyl(1,2,3-trihydro-4-keto-1,1,6,10-tetramethylnaphthalene; 4-Methyl-1,6-di(1,1,5-trimethyl-4-keto-5-cyclohexenyl)-1,3,5-hexatriene; 3,7-Dimethyl-8-tolunyl-1-(1,1,5-trimethyl-keto-5-cyclohexenyl)-1,3,5,7-octatetraene; 3,6,10-trimethyl-1,12-bis(1,1,5-trimethyl-4-keto-5-cyclohexenyl)-1,3,5,7,9,11-dodecahexaene; 6,10-Dimethyl-1,12-bis(1,1,5-trimethyl-4-keto-5-cyclohexenyl)-1,3,5,7,9,11-dodecahexaene.

This study is the first on canthaxanthin thermal degradation. The presence of all of the above compounds as canthaxanthin thermal decomposition products have not been reported in the literature.

ACKNOWLEDGEMENTS

The author wishes to extend his gratitude to his major advisor, Dr. Henryk Dann for his guidance, advice, encouragement and invaluable direction during my work on this dissertation.

The author's special gratitude goes to his committee member Dr. Elizabeth F. Stier, the Graduate Program Director of the Food Science Department. She was so untiring, generous and unsparing with her time and advice during all my years in this department. I am deeply indebted for her unfailing interest and support which actually started one year before I was admitted to the University in 1978. So many of us owe so much to Dr. Stier.

The author also wishes to thank his committee member, Dr. Chi-Tang Ho, Food Science Department, for his helpful insights, ideas and advice and especially for permitting the use of his laboratory instruments.

The author extends his thanks and appreciation to his outside committee member, Dr. Perry S. Manchand from Hoffman-LaRoche, Inc. for all of his help, valuable suggestions, and for supplying the canthaxanthin pigment which was used in this research.

Hoffman-LaRoche, Inc. were their usual generous and willing supplier of samples critical to the completion of

this research.

The author also wishes to thank both his uncle and his aunt, Dr. Mahmoud F. Bishr and Dr. N. O. Bishr for their support and encouragement for the achievement of the goal.

The author also wishes to thank both Dr. Thomas Hartman and Dr. Robert Rosen for their great help during the GC-MS analysis and their invaluable assistance.

The author also wishes to thank Mr. Robert Markley for his continued and cheerful readiness to offer all the needed help.

Finally, I wish to express my deep appreciation to the Center for Advanced Food Technology (CAFT) for their generous contribution covering part of the cost of the mass spectrometric analysis.

New Jersey Agricultural Experiment Station, Publication No. T-10100-18-86 supported by state funds and the U.S. Hatch Act.

SPECIAL THANKS

TO

MY WIFE

My wife Constance E. Roshdy, whom I deeply love, was a constant source of inspiration, moral support and encouragement. For her great patience and assistance especially in reviewing and typing this dissertation, I thank her from the bottom of my heart.

DEDICATION

This work is dedicated to my great and lovely mother, who was selected as the Model Mother for my high school in Cairo, Egypt in 1963. With love, support, encouragement and wisdom she lit the way to this achievement.

TABLE OF CONTENTS

	PAGE
ABSTRACT	ii
ACKNOWLEDGEMENTS	iv
SPECIAL THANKS	vi
DEDICATION	vii
 1. INTRODUCTION	 1
 2. LITERATURE REVIEW	 3
2.1. Occurrence of oxycarotenoids	3
2.1.1. In Foods	3
2.1.2. In Fish	4
2.1.3. In Crustacea	10
2.1.4. In Birds	13
2.1.5. In Meat	13
2.1.6. In Algae	14
2.2. Chemistry of Canthaxanthin	15
2.2.1. Molecular Structure	15
2.2.2. Chemical and Physical Properties	15
2.3. Applications of Canthaxanthin	18
2.3.1. Foods	18
2.3.2. Pharmaceutical Uses	26
2.4. Changes Occuring in Carotenoids	

During Processing	28
2.4.1. Baking	28
2.4.2. Canning	28
2.4.3. Dehydration-Drying	29
2.4.4. Cooking	30
2.4.5. Sterilization	30
2.4.6. Frying	31
2.4.7. Changes During Storage	32
2.4.8. Irradiation	32
2.5. Thermal Degradation of Carotenoids	35
2.6. Analysis of Volatile Degradation Products	33
3. HYPOTHESIS	41
4. RESEARCH OBJECTIVES	42
5. EXPERIMENTAL PROCEDURES	43
5.1. Equipment and Materials	43
5.2. Heating of Glycerol	46
5.3. Heating Canthaxanthin in Glycerol	46
5.4. Analysis of the Volatile Thermal Degradation	
Products (TDP) of Heated Canthaxanthin	51
5.4.1. Extraction Procedures	51
5.4.1.1. Sample Preparation	51
5.4.1.2. Initial Concentration	51

5.4.1.3. Final Concentration	52
5.4.2. Quantitative Analysis	52
5.4.3. Qualitative Analysis	53
5.5. Analysis of The Non-volatile Thermal	
Degradation Products of Heated Canthaxanthin .	54
5.5.1. Sample Preparation	54
5.5.1.1. Extraction Procedures	54
5.5.1.2. Evaporation of Ethyl Acetate	55
5.5.2. Canthaxanthin Determination	55
5.5.3. Reverse-Phase (HPLC) Analysis	56
5.5.3.1. Sample Preparation	56
5.5.3.2. Isolation and Collection	57
5.5.3.3. Analytical HPLC	58
5.5.3.4. 1st Preparative Separation	59
5.5.3.5. Evaporation of the Solvents	59
5.5.3.6. 2nd Preparative Separation	60
5.5.3.7. Evaporation of the Solvents	60
5.5.4. Spectroscopic Analysis	60
5.5.4.1. UV-Visible Spectrophotometry	60
5.5.4.2. Infrared Spectrometry	61
5.5.4.3. Mass Spectrometry	61
6. RESULTS AND DISCUSSION	62
6.1. Observations After Heat Treatments	62
6.2. Gas Chromatographic Analysis	64