UTILIZATION OF FATTY MATERIALS

IN

THE PREPARATION OF OXYGENATED COMPOUNDS

(EPOXY AND HYDROXY)

Thesis

Submitted in partial fulfillment for

the Degree of Master of Science

BY

FATMA ABD EL-HAFIZ BASSYOUNI

(B.Sc. Special Chemistry)

Ain Shams University

College of Girls,

National Research Center - Cairo

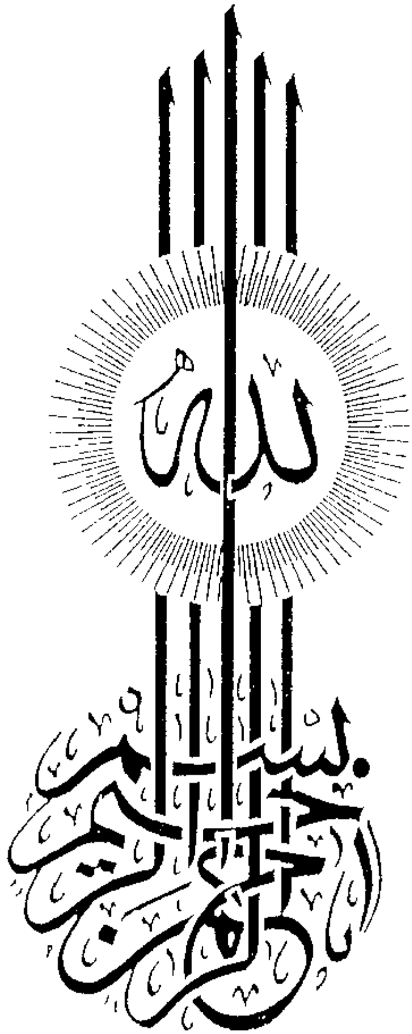
(1 9 9 1)

الله

بسم الله الرحمن الرحيم

قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا
عَلَّمْتَنَا إِنَّكَ أَنْتَ الْعَلِيمُ الْحَكِيمُ .

صدق الله العظيم
البقرة - ٣٢ -


بسم الله الرحمن الرحيم

UTILIZATION OF FATTY MATERIALS

IN

THE PREPARATION OF OXYGENATED COMPOUNDS

(EPOXY AND HYDROXY)

Thesis Supervisors

Prof. Dr.NADIA GHARIB KANDILE N. G. Kandile

Prof. Dr.MOHAMED M.H. EL-MALLAH M. El Mallah

Ass.Prof.Dr.SAFINAZ M.EL-SHAMI S. El-Shami

Prof.Dr.Marguerite Anis Wassef

Head of Chemistry Department

Marguerite A. Wassef

NOTE

The candidate has attended courses for one year, covering the following topics :

1. Photochemistry.
2. Spectroscopy.
3. Natural products
4. Quantum chemistry.
5. Thermodynamics.
6. Kinetics.
7. Instrumental analysis
8. Reaction Mechanism
9. Organometallic chemistry.
10. Heterocyclic chemistry.

She has successfully passed a written examination in these courses, in partial fulfillment for the degree of Master of science.

Approved

Vice - dean for Graduate Studies

ACKNOWLEDGMENT

The author wishes to express her sincere thanks and appreciation to prof . Dr. **NADIA GHARIB KANDILE**, Chemistry Dept., College for Girls, Ain Shams University for her kind helpful advice, criticism and guidance throughout the preparation of this work.

Thanks are also given to prof. Dr. **MARGUERITE ANIS WASSEF**, Head chemistry Dept. College for Girls, Ain Shams University, for her interest and encouragement.

The author is greatly indebted to prof. Dr. **M. HASSAN El - MALLAH**, Fats and Oils Res. Dept., NRC, Cairo, for suggesting the topic of this work and for his supervision, valuable guidance and helpful discussions.

Special thanks are extended to Ass. Prof Dr. **SAFINAZ M. EL - SHAMI**, Fats and Oils Res. Dept., NRC, Cairo, for her cooperation in supervision, helpful criticism and assistance received in many ways.

The author wishes to thank Mr. **T. MURUI**, chief chemist, Research laboratory of N.O.M.,Yokohama, Japan, for his cooperation in the analysis of different samples.

Thanks are also expressed to **NATIONAL RESEARCH CENTRE**, Cairo, Egypt for providing all the facilities that made this work possible.

CONTENTS

SUMMARY

This work is divided into:

1 - General introduction and aim of work.

2 - Review of literature and two sections dealing with epoxidation and hydroxylation reactions of the fatty materials.

3 - Two experimental parts (Part I and Part II) dealing with epoxidation and hydroxylation of fatty materials.

General introduction deals with a general outlook of the importance of epoxidized and hydroxylated fatty materials as oxygenated oleochemicals for different industrial purposes (plastics, paints, greases, urethane foams, etc.). It is designed to study epoxidation as well as hydroxylation reactions as routes for the utilization of high-acidity rice bran oil (RBO) in the preparation of oxygenated compounds, namely, epoxy and hydroxy esters which are imported for the need of different industrial purposes. Model substances such as soybean oil and methyl oleate are also subjected to epoxidation and hydroxylation, and their optimum reaction conditions are taken as guide for reactions with RBO. It is noteworthy that RBO is produced annually in tonnages and is considered as potential fatty material for preparing different oxygenated compounds. In addition, the courses of these reactions are extensively studied with the help of programmed temperature gas chromatography (PTGC) in combination with the advanced methods of analysis, namely mass- and ^{13}C NMR spectrometry. This new trend is more advantageous than that conventionally used since it is able to follow the formation of different structures as well as different side reactions.

<u>Review of literature</u> : comprises several publications that deal with epoxidation and hydroxylation under different reaction conditions. Also, applications of epoxidized and hydroxylated fatty materials in different industrial purposes are also included.

<u>Part I</u> :

Part I of this work deals with studies on the course of epoxidation with the help of PTGC and GC-MS. Soybean oil (SBO), is selected as model olefin using the <u>in</u>-<u>situ</u> formed and preformed peracetic acid epoxidation. Conventional as well as the advanced methods of analysis are used to follow the course of epoxidation to obtain more information on such reaction. Concerning the conventional methods of analysis, oxirane ring (epoxy group) as well as residual unsaturation determinations are carried out from which epoxide yield is calculated.

Following the course of preformed peracetic epoxidation by PTGC, it is found necessary to convert the epoxidized soybean oil, prior to analysis, into methoxy-hydroxy ester derivatives by ring opening of the formed epoxides. This trend, adopted in the present work, has not yet been used as far one knows, in studying the course of this reaction. PTGC and GC-MS show the formation of five derivatives, namely, methoxy -hydroxy oleate (MHO), methoxy-hydroxy stearate (MHS).

epoxy, methoxy-hydroxy stearate (E_pMHS), epoxy dihydroxy stearate (E_pDHS) and dimethoxy-dihydroxy stearate(DMDHS). The two former compounds correspond to epoxy-oleate and epoxy-stearate, whereas the latter three correspond to diepoxy-stearate isomers. The epoxidation reaction of different unsaturates as well as the corresponding methoxy and hydroxy derivatives are illustrated.
It is found that total epoxides, in terms of their methoxy-hydroxy derivatives, reach a yield of 74.9% after 30 minutes and corresponds to 89.2% unsaturates conversion.
It is concluded that the course of epoxidation is preferably followed by the PTGC and GC-MS of the methoxy-hydroxy derivatives instead of the original epoxides.

When the catalytic <u>in situ</u> epoxidation of SBO is followed by conventional and advanced methods of analysis, it is found that longer reaction periods of 4 hours are required for this reaction. It is found that oxirane oxygen percentage reaches its maximal value of 6.3 after 4 hours, corresponding to 93.6% unsaturates conversion.

PTGC and GC-MS of the methoxy-hydroxy derivatives of the formed epoxides, show the presence of the same five components previously reported but in different proportions. A maximum yield of 75.2% epoxides, in terms of methoxy-hydroxy components, is obtained which corresponds to 89.5% unsaturates conversion.

Four graphical representations of the course of the epoxidation of SBO with the preformed and <u>in situ</u> formed peracetic acid followed by conventional and advanced methods, are illustrated.

From the results of epoxidation of SBO selected as model substance, it is found that in situ epoxidation is suitable for the epoxidation of rice bran oil as a route for its utilization as a cheap source for oleochemicals preparation. The in situ method is selected, due to the fact that the preformed peracetic acid requires 15-24 hours for its preparation and two more hours for epoxidation.

The rice bran oil is dewaxed and then converted into butyl esters, since the crude oil contains appreciable amounts of free fatty acids, partial glycerides. It is found advisable to follow directly the epoxy-esters formed during the course of epoxidation since it is believed that butyl epoxy esters are more stable than the methyl esters during PTGC. the course of the reaction is followed by the conventional and advanced methods of analysis.

Conventional methods of analysis show that a maximum oxirane oxygen of 4.5% (81.0% epoxides) can be obtained after 4 hours. This yield corresponds to 86.7% unsaturates conversion.

Following the course of epoxidation with PTGC, it is found that the epoxy-esters formed during epoxidation are epoxy-oleate (E_pO), epoxy-stearate (E_pS) and diepoxy-stearate diasterioisomers (liquid and solid isomers) DE_pS (L) and DE_pS (S). It is noteworthy that epoxy-butyl esters are directly determined by PTGC (not as their methoxy-hydroxy-derivatives) due to the fact that RBO butyl esters contain higher oleate and lower linoleate than SBO and accordingly.

no difficulties are encountered with the epoxy-esters determination. Standard epoxy-esters are used in their identifications. It is concluded that the total epoxy esters reaches a maximum of 78.5% after 4 hours corresponding to 91.4% unsaturates conversion. It is also found that linoleate responds to epoxidation at higher rate than oleate. Therefore, rice bran oil can be utilized as a cheap source for the preparation of epoxy esters to be used in the field of plasticizer-stabilizer for PVC or as plasticizer in paints.

Part II :

This part deals with the study of the courses of mono- and di-hydroxylation of fatty materials using the advanced methods of analysis to follow the formation of hydroxy products with the confirmation of their structures. This new trend is of importance, since, it throws light on the hydroxylation as well as the accompanied side reactions that can not be easily detected by the conventional methods of analysis. In addition, it is aimed to utilize high_acidity rice bran oil in the preparation of hydroxy acids. This part is divided into two sections, namely Section 1 which deals with dihydroxylation and Section 2 which deals with monohydroxylation.

Section 1 deals with the studies on the course of resin catalyzed dihydroxylation of fatty materials. Methyl oleate, selected as model olefin, is subjected to dihydroxylation using two selected strong acid cation exchangers, namely, Amberlite IR-120 (gel type) and Lewatit SP-120