شبكة المعلومات الجامعية

بسم الله الرحمن الرحيم

شبكة المعلومات الجامعية

التوثيق الالكتروني والميكروفيلم

شبكة المعلومات الجامعية

جامعة عين شمس

التوثيق الالكتروني والميكروفيلم

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بالرسالة صفحات لم ترد بالاصل

Cairo University

Faculty of Science
Department of Chemistry

Synthesis of Some Fat Based Heterocycles from Olive Oil Production Waste Precursors

A Thesis
Submitted for

The Ph. D. Degree in Organic Chemistry

By
Hanaa Mohammed Soliman Hasan

(M. Sc. Cairo university, 2002)

Department of Chemistry
Faculty of Science
Cairo University
Giza, Egypt

2010

بسم الله الرحمن الرحيم

سبحانك لا علم لنا إلا ما علمتنا

إنك أنت العليم الحكيم

APPROVAL SHEET FOR SUBMISSION

Title of the Ph.D. Thesis:

Synthesis of Some Fat Based Heterocycles from Olive Oil Production Waste Precursors

Name of Candidate: **Hanaa Mohamed Soliman Hasan**

This Thesis has been approved for submission by Supervisors:

SUPERVISORS — *Signature*

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2. **Dr. Mohmed R. Shaban**
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ABSTRACT

Title of the Ph.D. Thesis:

Synthesis of Some Fat Based Heterocycles from Olive Oil Production Waste Precursor

Name of Candidate: **Hanaa Mohamed Soliman Hasan**

Degree: (Ph. D.) Unpublished Ph. D. of Science Thesis, Faculty of Science, Cairo University, 2010.

This work has been carried out to investigate the utility of methyl octadecenoate for the synthesis of some new heterocyclic compounds pended to long chain fatty acid residue such as triazole, pyrazole, thiadiazole, thiadiazine, oxadiazole, 1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazole, triazalo[2,1-b]-1,3,4-thiadiazole, 1,2,4-triazolo[3,4-*b*]benzo[1,2-*d*]-1,3-oxazine, benzyo[1`,2`-4,5]imidazo[1,2-*c*]triazole, 1,2,4-triazolo[1,5-*a*]pyrimidine, 1,2,4-triazolo[1,5-*a*]pyrimidine, imidazo[1,2-b][1,2,4]triazole, 1,3,4-triazolo[1,5-*a*]pyrimidine, [1,2,4]triazolo[5,1-*c*][1,2,4]triazine, 1,2,4-triazolo[1,5-*c*]pyrido[2`,3`-*e*]-1,3,4-triazine, 1,2,4-triazolo[1,5-*c*]pyrimido[5`,4`-*e*]-1,3,4-triazine, 1,2,4-triazolo[5,1-*c*]-pyrazino[4,3-*e*]1,2,4-traizine, pyrazolo[5,1-c][1,2,4]triazine, and 1,2,4-triazolo[3,4-c][1,2,4]triazole derivatives of expected potential biological activity.

Key Words: 1,2,4-triazolo[3,4-*b*]benzo[1,2-*d*]-1,3-oxazine, 1,2,4-triazolo[1,5-*a*]pyrimidine, 1,2,4-triazolo[1,5-*c*]pyrido[2`,3`-*e*]-1,3,4-triazine, 1,2,4-triazolo[5,1-*c*]-pyrazino[4,3-*e*]1,2,4-traizine, 1,2,4-triazolo[1,5-*a*]pyrimidine, imidazo[1,2-b][1,2,4]triazole.

SUPERVISORS

1. Prof. Dr. Ahmed Mahmoud Farag A. M. Farag

2. Dr. Mohmed R. Shaban

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Finally, the author would like to express her appreciation to all who make possible the completion of this work in its final form.

Hanaa Mohamed Soliman

إهـــداء

إلى أبي الغالي

وروح أمي الحبيبة

وزوجي العزيز

وأخواتي

وابني

CONTENTS

I. AIM OF THE PRESENT WORK

I. AIM OF THE PRESENT WORK

Production of olive oil is one of the important industries in Egypt. The rate grows rapidly each year.

The pomace left over from olive oil processing can be used as organic fertilizer, animal food and as a source of energy. It also used to produce crude pomace olive oil (low grade olive oil), It can be also utilized to produce oleic acid which can be used for production of several derivatives of important industrial application such as esters, amides, epoxides, and metallic soap. Oleic acid methyl ester can be used as versatile starting material for preparation of a variety of heterocyclic ring systems attached to long chain fatty acid residue. Such new compounds are supposed to have potent biological activity of beneficial effect on human health. In addition, they have several advantages over the parent heterocyclic compounds. They can easily penetrate the lipoprotein cell membrane, and they can be stored in the liver as a lipid component that can be used whenever it is needed. Also, the toxic and side effects of the heterocyclic compounds can be reduced by the presence of the long fatty acid chain acting as a tail. Use can be made of the dual biological effects of both fatty acid and heterocyclic compound. Selection of the type of fatty acid as well as the type of heterocyclic ring system can be properly made as to realize the production of a certain compound of a strong desirable biological function.

The present study was undertaken to explore the utility of oleic acid methyl ester for the synthesis of a variety of heterocyclic systems pendant to a long chain fatty acid residue. Examples of the target compounds are methyl octadec-9-noate **(1)**, octadec-9-enylhydrazide **(2)**, 1-octadec-9-enoyl-4-phenylthiosemicarbazide **(4)**, 5-heptadec-8-enyl-4-phenyl-2*H*-

1,2,4-triazole-3(4*H*)-thione **(5)**, 5-heptadec-8-enyl-*N*-phenyl-1,3,4-thiadiazole-2-amine **(6)**, 3-heptadec-8-enyl-5-(methylthio)-4-phenyl-4*H*-1,3,4-triazole **(7)**, 1-5-heptadec-8-enyl-4-phenyl-4*H*-1,2,4-triazol-3-yl)hydrazine **(8)**, ethyl 4-aryl-4,5-dihydro(-5-octadec-9-eneoylimino)-1,3,4-thiadiazole-2-carboxylate **13a-b**, (3-aryl-*N*-5-(phenylcarbamoyl)-1,3,4-thiadiazol-2(3*H*)-ylidene)octadec-9-enehydrazide **15a-c**, *N*-(3-aryl-5-substituted-1,3,4-triazol-2(3*H*)-ylidene)octadec-9-nehydrazide **16a-d**, (5-heptadec-8-enyl-2-phenylamino-4*H*-1,3,4-thiadiazin-6-yl)(Aryl) methanone **20a-c**, (5-alkyl-2-(phenylamino)-4*H*-1,3,4-thiadiazin-6-yl)octadec-9-en-1-one **22a-b**, 5-heptadec-8-enyl-2-phenylamino-4*H*-1,3,4-thiadiazine-6-carbonitrile **(26)**, 5-(heptadec-8-enyl)-1,3,4-oxadiazole-2(3*H*)-thione **(28)** and 5-(heptadec-8-enyl)-1,3,4-thiadiazole-2(3*H*)-thione **(29)**, 5-(heptadec-8-enyl)-1,3,4-oxadiazol-2(3*H*)-one **(31)**, 4-aryl-4*H*-5-heptadec-8-enyl-2*H*-1,2,4-triazole-3(4*H*)-thione **32a-d**, 4-amino-3-substituted-5-heptadec-8-enyl-1,2,4-triazole **33a-b**, 1-Amino-1*H*-5-heptadec-8-enyl-3-methylthio-1,3,4-triazole **(34)**, bis-3-heptadec-8-enyl-5-triazalo[2,1-*b*]-1,3,4-thiadiazole **(35)**, 3-heptadec-8-enyl-1,2,4-triazolo[3,4-*b*]-1,3,4-thiadiazole **(36)**, 5-heptadec-8-enyl-4-hydroxy-4*H*-3-substituted-1,2,4-triazole **37a-b**, 3-(heptadec-8-enyl)oxazolo [2,3-*c*] [1,2,4]triazol-6(5*H*)-one **(38)**, 3-(heptadec-8-enyl)-1,2,4-triazolo[3,4-*b*]benzo[1,2-*d*]-1,3-oxazin-9-one **(39)**, 2-heptadec-8-enyl-benzyo[1`,2`-4,5]imidazo[1,2-*c*]triazole **(40)**, 5-(heptadec-8-enyl)-1*H*-1,2,4-triazol-3-amine **(41)**, 7-heptadcanyl-2-(heptadec-8-enyl)-[1,2,4]triazolo[1,5-*a*] pyrimidine-6-carbonitrile **(46)**, 2-(heptadec-8-enyl)-7-methyl-1,2,4-triazolo[1,5-*a*]pyrimidin-5(4*H*)-one **(49)**, *N*-(2-(3-(heptadec-8-enyl)-1*H*-1,2,4-triazol-1-yl)-1-arylethylidene) methanamine **51a-c**, 6-amino-2-heptadec-8-enyl-1,3,4-triazolo[1,5-*a*]pyrimidin-5(4*H*)-one **(54)**, diazonium salt of the aminotriazole **55**, 4-amino-7-heptadec-8-enyl-