

STUDIES ON SOME COUMARIN DERIVATIVES

A Thesis

Submitted For The Degree Of Doctor Philosophy
(Ph.D. in Chemistry)

Presented By

Souad Abdel-Aziz El-Metwally

(B.Sc. and M.Sc. in Chemistry)

Supervised By

Prof. Dr. Mohamed Ali Hassan

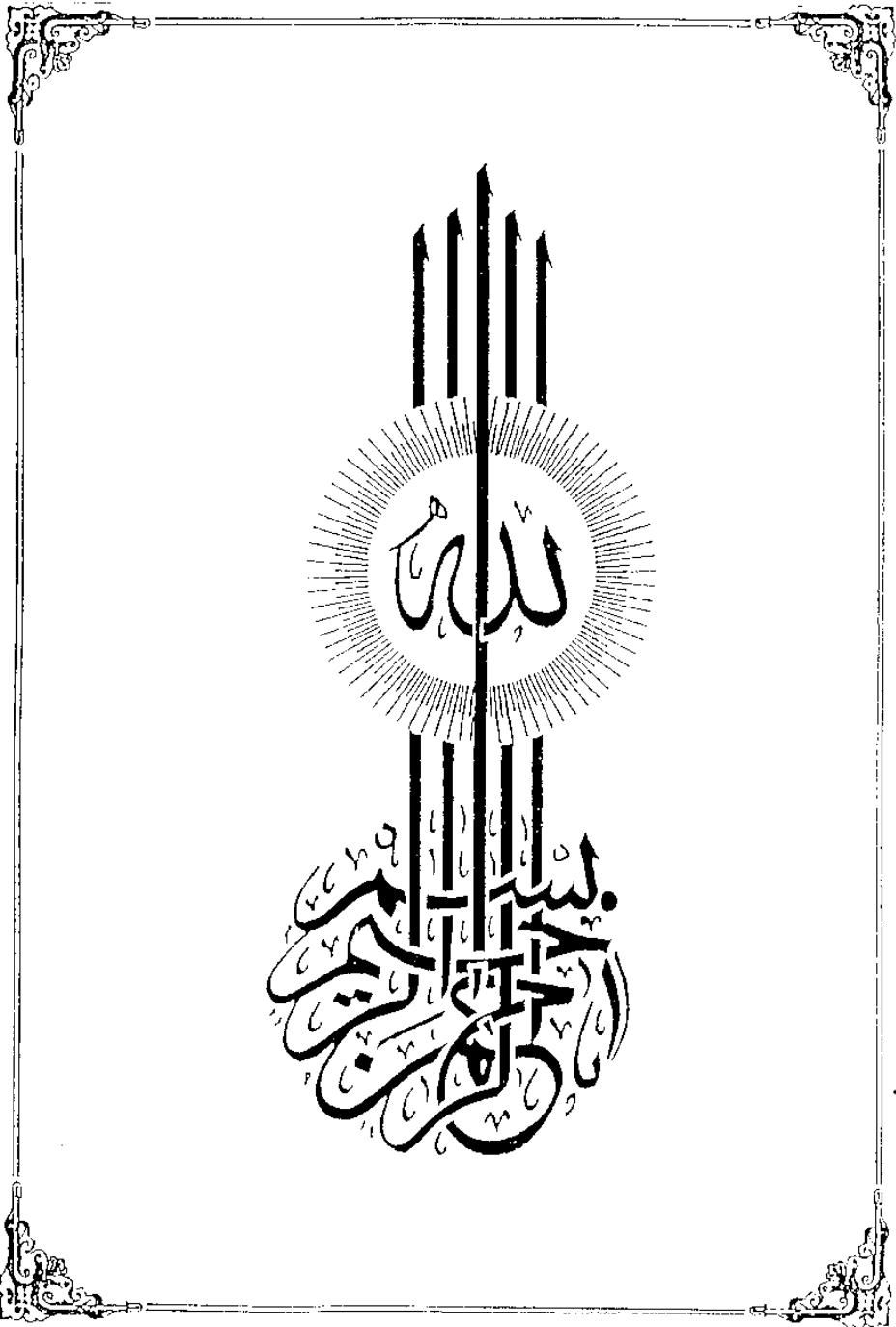
Dr. Sayed Ahmed Shiba

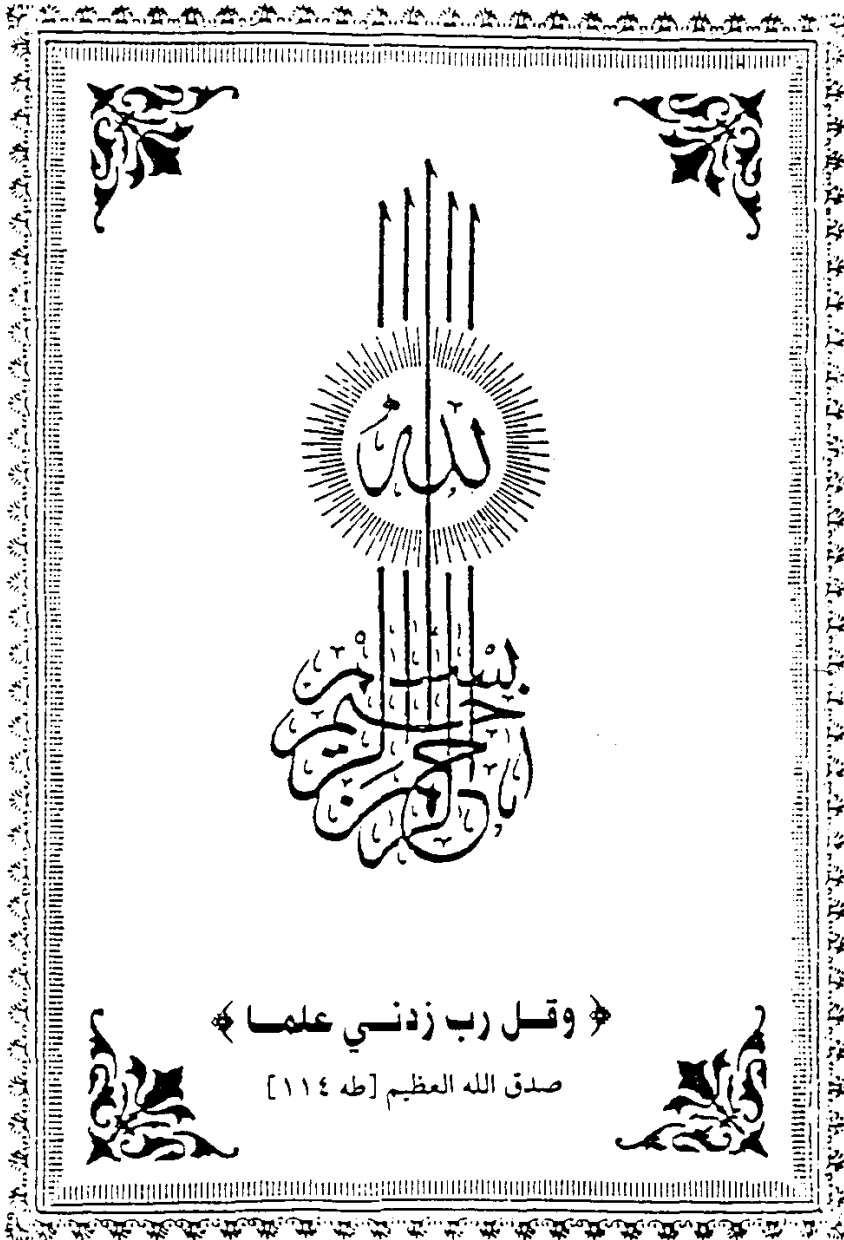
Dr. Nagwa Mohamed S. Harb

Dr. Mohsen Mohamed K. Abuo El-Regal

*Faculty Of Science
Ain Shams University
Cairo, Egypt*

1997





﴿وقل رب زدني علما﴾

صدق الله العظيم [طه ١١٤]

STUDIES ON SOME COUMARIN DERIVATIVES

Presented By
Souad Abdel-Aziz El-Metwally
(B.Sc. and M.Sc. in Chemistry)

THESIS ADVISORS

THESIS APPROVED

Prof.Dr. Mohamed Ali Hassan.....*M. A. Hassan*
Dr. Sayed Ahmed Shiba.....*S. Shiba*
Dr. Nagwa Mohamed S. Harb.....*Nagwa Harb*
Dr. Mohsen Mohamed K. Abuo El-Regal.....*M. K. Abou El Regal*

Head Of Chemistry Department

A. F. M. Fahmy
Prof. Dr. A.F.M. Fahmy

ACKNOWLEDGEMENT

I would like to express my sincere gratitude and indebted to **prof. Dr. Mohamed Ali Hassan**, *professor of Organic Chemistry*, Chemistry Department, Faculty of Science, Ain Shams University. He was always kind enough to suggest the lines of research and to follow the progress of the work with keen interest, guidance and valuable criticism.

Also, I wish to acknowledge my sincere gratitude to **Dr. Sayed Ahmed Shiba**, *assistant professor*, **Dr. Nagwa Mohamed Harb**, *assistant professor* and **Dr. Mohsen Mohaned Kamal Abuo El-Regal**, *Lecturer*, Chemistry Department, Faculty of Science, Ain Shams University for their kind and valuable help, encouragement, meticulous supervision, continuous advices and their efforts to evaluate this humble work for success.

I would like to express my appreciation and gratitude to **Prof. Dr. D.DOEP**, *profesor of Organic Chemistry*, Institute of Organic Chemistry, Duisburg University, GERMANY, for his kind and great helps to carry out the elemental analysis and IR, NMR, MS spectral measurements of most of my products in his Department.

CONTENTS

	Page
List of Tables.....	i
List of Figures.....	ii
Summary of the original work.....	vii
Introduction.....	1
Synthesis of coumarins	1
Reactions of coumarins	23
Discussion of the original work.....	
Part-I: Synthesis and reactions of.....	59
3-carbethoxy-5,7-dimethoxycoumarin.....	
Part-II: Synthesis and reactions of.....	88
some methylcoumarins.....	
Experimental.....	118
References.....	131

LIST OF TABLES

Table No.	Page
1- Physical data of compounds 2,3,4 and 5	120
2- Physical data of compounds 3,6 and 7	121
3- Physical data of compounds 8 and 9	121
4- Physical data of compounds 15 and 16	124
5- Physical data of compounds 21a,b	126
6- Physical data of compounds 22 and 23	127
7- Physical data of compounds 24, 25, 26 and 27	128
8- Physical data of compounds 28a,b; 30a,b; 32a,b; 33a,b; 34; 35 ; 36 and 37	129
9- Physical data of compounds 29 and 31	130

List of figures

- Fig.1: ^1H -NMR spectrum (CDCl_3) of 3-carbethoxy-5,7-dimethoxycoumarin (1).
- Fig.2: ^1H -NMR spectrum (CDCl_3) of 3-carbethoxy-5,7-dimethoxy-4-dicynomethyl-3,4-dihydro-5,7-dimethoxycoumarin (2).
- Fig.3: Mass spectrum of 3-carbethoxy-5,7-dimethoxy-4-dicynomethyl-3,4-dihydro-5,7-dimethoxycoumarin (2).
- Fig.4: ^1H -NMR spectrum (CDCl_3) of 10-carbethoxy-7,9-dihydroxy-1,3-dimethoxy-6-oxo-6H-dibenzo[b,d]pyran(3).
- Fig.5: ^1H -NMR spectrum (CDCl_3) of 5,7-dimethoxycoumarin-3-carboxylic acid (4).
- Fig.6: Mass spectrum of 5,7-dimethoxycoumarin-3-carboxylic acid (4).
- Fig.7: Mass spectrum of 1-acetyl-8,10-dimethoxy-2-methyl-4H,5H-pyrano[3,4-c]benzopyran-4,5-dione(5).
- Fig.8: Mass spectrum of 10-acetyl-7,9-dihydroxy-1,3-dimethoxy-6H-dibenzo[b,d]pyran-6-one (6).
- Fig.9: ^1H -NMR spectrum (CDCl_3) of 1-cyano-8,10-dimethoxy-2-ethoxy-4-hydroxy-4aH,5aH-pyrano[3,4-c]benzopyran-5-one (7).
- Fig.10: ^1H -NMR spectrum (CDCl_3) of 5,7-dimethoxy-4-(2-oxocyclohexyl)-2-oxo-1,2,3,4-tetrahydroquinolin-3-carboxamide (8).
- Fig.11: Mass spectrum of 5,7-dimethoxy-4-(2-oxocyclohexyl)-2-oxo-1,2,3,4-tetrahydroquinolin-3-carboxamide (8).

- Fig.12: ^1H -NMR spectrum (CDCl_3) of 5,7-dimethoxy-4-(2-oxocycloheptyl)-3,4-dihydrocoumarin-3-carboxamide (**9**).
- Fig.13: Mass spectrum of 5,7-dimethoxy-4-(2-oxocycloheptyl)-3,4-dihydrocoumarin-3-carboxamide (**9**).
- Fig.14: ^1H -NMR spectrum (CDCl_3) of 5,7-dimethoxycoumarin (**11**).
- Fig.15: Mass spectrum of 5,7-dimethoxycoumarin (**11**) compared with the library database (5,7-dimethoxy-2H-1-benzopyran-2-one).
- Fig.16: ^1H -NMR spectrum (CDCl_3) of 3-carbomethoxy-5,7-dimethoxycoumarin (**12**).
- Fig.17: ^1H -NMR spectrum(CDCl_3)of 5,7-dimethoxycoumarin-3-carboxamide (**13**).
- Fig.18: Mass spectrum of 5,7-dimethoxycoumarin-3-carboxamide (**13**).
- Fig.19: ^1H -NMR spectrum (DMSO) of 5,7-dimethoxycoumarin-3-(N-p-tolyl)-carboxamide (**14**).
- Fig.20: Mass spectrum of 2-hydroxy-4,6-dimethoxybenzalazine (**15**).
- Fig.21: ^1H -NMR spectrum(CDCl_3)of 5,7-dimethoxycoumarin-3-(N-phenyl)hydrazide (**16**).
- Fig.22: Mass spectrum of 5,7-dimethoxycoumarin-3-(N-phenyl)-hydrazide (**16**).
- Fig.23: Mass spectrum of 8-bromo-3-carbethoxy-5,7-dimethoxycoumarin (**17**).
- Fig.24: ^1H -NMR spectrum(CDCl_3)of 5,7-dimethoxy-2,2-diphenyl-3-(hydroxy-diphenyl)methyl-2H-[1]benzopyran (**18**).
- Fig.25: Mass spectrum of 5,7-dimethoxy-2,2-diphenyl-3-(hydroxydiphenyl)methyl-2H-[1]benzopyran (**18**).