

بسم الله الرحمن الرحيم



SALWA AKL



شبكة المعلومات الجامعية

التوثيق الالكتروني والميكروفيلم



SALWA AKL

جامعة عين شمس

التوثيق الإلكتروني والميكروفيلم

قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها
علي هذه الأقراص المدمجة قد أعدت دون أية تغيرات



يجب أن

تحفظ هذه الأقراص المدمجة بعيدا عن الغبار



SALWA AKL



بعض الوثائق الأصلية تالفة



SALWA AKL



بالرسالة صفحات

لم ترد بالأصل



SALWA AKL

B17393

**A Thesis Entitled
Chemical Studies On Certain Plants of
Family *Cruciferae***

**Submitted to
Chemistry Department
Faculty of Science
Cairo University**

**By
Khaled Abd El-Hady Abd El-Shafeek
B.Sc. in Chemistry
M.Sc. in Chemistry
Cairo University**

**For the Degree of
Doctor of Philosophy in Science**

***National Research Center
Cairo, Egypt
2002***

مستخلص

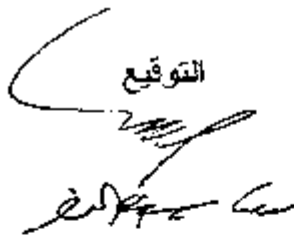
الاسم : خالد عبد الهادي عبد الشفيق

عنوان الرسالة : "دراسات كيميائية على بعض نباتات العائلة الصليبية"

الدرجة : دكتوراه الفلسفة في العلوم

الهدف من البحث : يهدف الى دراسة المكونات الكيميائية لنباتى القنبرة والملبحة (العائلة الصليبية) وقد تم فصل المركبات الفلافونيدية والجلوكوزيدات الكبريتية فى كلا النباتين ، حيث تم تعريف خمسة مركبات كمشتقات لاجليكون الكرستين وأربعة مركبات مشتقات لاجليكون الأيزورامينتين بالإضافة الى خمسة مركبات من الجلوكوزيدات الكبريتية . جرت دراسة الفاعلية البيولوجية للمستخلصات المختلفة لكلا النباتين وكذلك لبعض المركبات المفصولة من كل منهما .

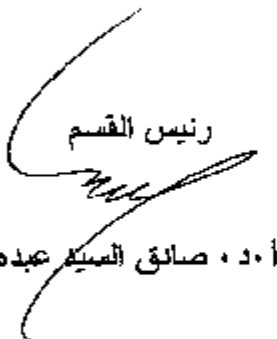
الكلمات الدالة : الكريكترا أتوا ، الفرزيتيا إيجيبتيا ، العائلة الصليبية ، فلافونيدات ، جلوكوزينولات ، مضاد للحشرات ، السمية والفارماكولوجية ، مضاد لمسارات جهاز المناعة .

التوقيع


المشرفين

أ.د. صادق السيد عبده

أ.د. مدحت محروس سيف النصر

رئيس القسم

أ.د. صادق السيد عبده

List of Published Papers during the work

- 1- Anew acylated flavonol triglycosides from *Carrichtera annua* .
Khaled A. Abdel-Shafeek; Moustafa M. El-Messiry; Abdel atty A. Shahat;
Sadara Apers; Luc Pieters and Medhat M. Seif –El Nasr.
J. Nat. Product, 63(6), 845-847, (2000).
- 2- Some toxicological and biochemical studies of the alcoholic extracts of
Carrichtera annua and *Farsetia aegyptia* on albino rats.
Scham A. El Batran; Khaled A. Abdel-Shafeek; Moustafa M. El-Messiry;
Medhat M. Seif –El Nasr and Mahmoud S. Arbid .
J. Egypt. Soc. Pharmacol. Exp. Ther. 20(1), 175-189,(2001).
- 3-Biological and insecticidal effects of total glucosinolates and different extracts
of *Carrichtera annua* and *Farsetia aegyptia* on *Spodoptera littoralis* .
Ismail A. Ismail; Khaled A. Abdel-Shafeek; Moustafa M. El-Messiry and
Medhat M. Seif –El Nasr.
Bull. Nat. Res. Center (in press).

Contents

Item	Page
Summary	1
Introduction	4
Review of literature	6
I-Glucosinolates	6
1.1 Occurrence	6
1.2 Structure	17
1.3 Nomenclature	17
1.4 Enzymatic hydrolysis	18
1.5 Nonenzymatic hydrolysis	21
1.6 Biosynthesis	21
1.7 Isolation and separation	23
1.7.1 Column chromatography	23
a-Ion exchange column chromatography	23
b-Flash column chromatography	23
1.7.2 Paper chromatograph and high voltage electrophoresis.....	24
1.7.3 Thin layer chromatography	24
1.7.4 Gas chromatography	25
1.7.5 High performance liquid chromatography (HPLC)	26
1.8 Spectroscopic determination	26
1.8.1 Ultraviolet absorption spectra determination	26
1.8.2 Infrared spectroscopy	26
1.8.3 Mass spectroscopy	26
1.8.4 Fast Atom Bombardment mass spectroscopy (FAB-MS)	29
1.8.5 Gas chromatography/mass spectroscopy (GC/MS)	29
1.8.6 Nuclear Magnetic resonance (NMR)	29
1.9 Biological activity	31
1.9.1 Inhibition of chemical carcinogens	31
1.9.2 Fungistotic and bacterostatic effects	31
1.9.3 Effects on insects	32
1.9.4 Goitrogenicity	33
II -Flavonoids	34
Aim of work	44
The studied species	45
Plant material	48
Preliminary phytochemical screening	49
Experimental & Results	53
Extraction and fractionation of the flavonoidal constituents of	53
<i>C. annua</i>	53
Thin layer and paper chromatography	53

Item	Page
The UV absorption spectra measurements	56
Preparative paper chromatography of ethyl acetate fraction of <i>C. annua</i>	58
Purification of compound C-I	58
Identification of compound C-I	58
Purification of compound C-II	66
Identification of compound C-II	66
Purification of compound C-III	72
Identification of compound C-III	72
Column chromatographic fractionation of Butanol fraction of <i>C. annua</i>	76
Purification of compound C-IV	77
Identification of compound C-IV	77
Purification of compound C-V	110
Identification of compound C-V	110
Preparation of total glucosinolates of <i>C.annua</i>	115
Acidic aluminum oxide column chromatography	115
Cellulose column chromatography	115
Chromatographic investigation	116
Separation of glucosinolates by preparative paper chromatography	118
Purification of compound G-I	118
Identification of compound G-I	118
GC/MS analysis of the aglucone of compound G-I.....	121
Enzymatic hydrolysis of compound G-I	122
Purification of compound G-II	124
Identification of compound G-II	124
Investigation of the flavonoidal constituents of <i>F. aegyptia</i> Turra	126
Chromatographic investigation	126
Preparative chromatographic fractionation of the ethyl acetate fraction..	126
Purification of compound F-I	126
Identification of compound F-I	127
Purification of compound F-II	131
Identification of compound F-II	131
Column chromatographic fractionation of the Butanol fraction	143
Purification of compound F-III	144
Identification of compound F-III	144
Purification of compound F-IV	162
Identification of compound F-IV	162
Preparation of total glucosinolates of <i>F.aegyptia</i> Turra	172
Preparative paper chromatography of the total glucosinolates	172
Purification of compound E-I	172
Identification of compound E-I	173
Purification of compound E-II	175
Identification of compound E-IIA	175

Item	Page
Identification of compound E-IIB	177
Biological evaluation	179
1-Pharmacotoxicity and pharmacological studies.....	179
Materials and methods	179
a-Preparation of the alcoholic extracts	179
b-Diagnostic kits	179
c-Test animals	179
Determination of LD ₅₀ of different extracts	179
Clinical symptoms and mortality	180
Post-mortem findings	181
Biochemical assay	182
Statistical analysis	182
2-Anti-complement activity study	184
Introduction	184
Terminology	186
Complement components	186
The classical pathway	186
The alternative pathway	186
How to detect and measure complement	187
Complement modulation assay	187
Hemolytic assay	188
Preparation of test solution	189
3- Insecticidal activity studies	191
Introduction.....	191
Material and methods	191
Test insect	191
Extraction of plant materials and isolation of total glucosinolates	191
Insecticidal activity	192
Ovicidal activity	192
Antifeedant activity	192
Ovipositional inhibitory effect (Non choice test)	193
Ovipositional inhibitory effect (Choice test)	193
Developmental effect	193
Results	194
Discussion	202
References	206
Arabic summary	223

List of figures

Fig. No.	Page
Fig. (1) : <i>Carrichtera annua</i> (L.) DC	46
Fig. (2) : <i>Farsetia aegyptia</i> Turra	47
Fig. (3) : UV absorption spectra of compound C-I	59
Fig. (4) : Positive ion FAB- mass spectrum of compound C-I	61
Fig. (5) : EI-mass spectrum of compound C-I	62
Fig. (6) : ¹ H-nmr spectrum (DMSO) of compound C-I	63
Fig. (7) : ¹³ C-nmr spectrum (DMSO) of compound C-I	64
Fig. (8) : UV absorption spectra of compound C-II	67
Fig. (9) : Negative ion FAB-mass spectrum of compound C-II	69
Fig. (10) : ¹ H-nmr spectrum (DMSO) of compound C-II	70
Fig. (11) : UV absorption spectra of compound C-III	73
Fig. (12) : Negative ion FAB- mass spectrum of compound C-III	75
Fig. (13) : UV absorption spectra of compound C-IV	78
Fig. (14) : Negative ion FAB- mass spectrum of compound C-IV	80
Fig. (15) : ¹ H-nmr spectrum (DMSO) of compound C-IV	81
Fig. (16) : ¹³ C-nmr spectrum (DMSO) of compound C-IV	84
Fig. (17) : DEPT-135 spectrum of compound C-IV	88
Fig. (18) : DEPT- 90 spectrum of compound C-IV	89
Fig. (19) : HMBC spectrum of compound C-IV	91
Fig. (20) : TOCSY spectrum of compound C-IV	97
Fig. (21) : HSQC spectrum of compound C-IV	102
Fig. (22) : DQF-COSY spectrum of compound C-IV	105
Fig. (23) : UV absorption spectra of compound C-IV	111
Fig. (24) : Positive ion FAB mass spectrum of compound C-V	113
Fig. (25) : ¹ H-nmr spectrum (DMSO) of compound G-I	119
Fig. (26) : ¹³ C-nmr spectrum (DMSO) of compound G-I	120
Fig. (27) : EI-mass spectrum of the aglucone of compound G-I	123
Fig. (28) : EI-mass spectrum of the aglucone of compound G-II	125
Fig. (29) : UV absorption spectra of compound F-I	128
Fig. (30) : EI-mass spectrum of compound F-I	130
Fig. (31) : UV absorption spectra of compound F-II	132
Fig. (32) : Negative ion FAB- mass spectrum of compound F-II	134
Fig. (33) : ¹ H-nmr spectrum (DMSO) of compound F-II	135
Fig. (34) : ¹³ C-nmr spectrum (DMSO) of compound F-II	138
Fig. (35) : UV absorption spectra of compound F-III	145
Fig. (36) : Negative ion FAB- mass spectrum of compound F-III	147
Fig. (37) : ¹ H-nmr spectrum (DMSO) of compound F-III	148
Fig. (38) : ¹³ C-nmr spectrum (DMSO) of compound F-III	153
Fig. (39) : DEPT-135 spectrum of compound F-III	159

Fig. No.	Page
Fig. (40) : DEPT-90 spectrum of compound F-III	160
Fig. (41) : UV absorption spectra of compound F-IV	163
Fig. (42) : ^1H -nmr spectrum (DMSO) of compound F-IV	165
Fig. (43) : ^{13}C -nmr spectrum (DMSO) of compound F-IV	167
Fig. (44) : DEPT spectrum (DMSO) of compound F-IV	168
Fig. (45) : mass spectrum of compound E-I.....	174
Fig. (46) : mass spectrum of compound E-II A.....	176
Fig. (47) : mass spectrum of compound E-II B.....	178
Fig. (48) : pathways of the complement system	185
Fig. (49) : Insecticidal activity of tested extracts against 3 rd. instar larvae of <i>S. littoralis</i> at 5% concentration	195
Fig. (50) : Ovicidal activity of tested extracts at 5% concentration.....	197
Fig. (51) : Ovipositional effect of tested extracts against <i>S. littoralis</i> moths in choice and non choice treatments	200

List of tables

Table No.	Page
1- The glucosinolates isolated from family <i>Cruciferae</i>	7
2- The flavonoids isolated from family <i>Cruciferae</i>	36
3- Phytochemical screening of the studied plants	52
4- UV. absorption data for compound C-I.....	60
5- ¹ H and ¹³ C –nmr data for compound C-I.....	65
6- UV. absorption data for compound C-II.....	66
7- UV. absorption data for compound C-III.....	72
8- Column chromatography of butanol fraction of <i>C. annua</i>	76
9- UV. absorption data for compound C-IV.....	79
10- ¹ H and ¹³ C –nmr data for compound C-IV.	87
11- UV. absorption data for compound C-V.....	110
12- ¹³ C-nmr data of compound G-I.....	121
13- UV. absorption data for compound F-I.....	127
14- UV. absorption data for compound F-II.....	133
15- ¹³ C-nmr data of compound F-II.....	141
16- Column chromatography of butanol fraction of <i>F.aegyptia</i>	143
17- UV. absorption data for compound F-III.....	146
18- ¹³ C-nmr data of compound F-III.....	156
19- UV. absorption data for compound F-IV.....	162
20- ¹³ C-nmr data of compound F-IV.....	170
21- LD ₅₀ of the defatted alcoholic extract of <i>C. annua</i>	180
22- LD ₅₀ of the defatted alcoholic extract of <i>F.aegyptia</i>	181
23- Effect of different treatments on serum GGT,AST,ALT,creatinine and urea levels	183
24- IC ₅₀ (μ g/ml) values of tested fractions on the AP and CP of the complement system.....	190
25- Insecticidal activity of tested extracts against 3 rd . instar larvae of <i>S. littoralis</i> (at 5% conc.)	194
26- Ovicidal activity of tested extracts (at 5% conc.).....	196
27- Insecticidal activity of tested extracts against 4th. instar larvae of <i>S. littoralis</i>	198
28- Ovipositional repellent effect of tested extracts against <i>S. littoralis</i> moths in choice and non choice tests.....	199
29- Effect of tested extracts on the development of <i>S. littoralis</i>	201

List of schemes

Scheme No.	Page
1- Hydrolysis products of glucosinolates by myrosinase.....	18
2- Hydrolysis products of γ -hydroxy glucosinolates by myrosinase.....	19
3- Hydrolysis products of indole glucosinolates by myrosinase.....	20
4- Non -enzymatic hydrolysis products of glucosinolates.....	21
5- The biosynthetic pathway of glucosinolates.....	22
6- CIMS fragmentation sites of glucosinolates.....	28
7- Numbered carbon skeleton of glucosinolates.....	30