

# การศึกษาทางพฤกษเคมีของดอกกระถินทุ่ง



ร้อยตำรวจโทหญิงสุชาดา สุขหรั่ง

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญา เกษศาสตรมหาบัณฑิต

ภาควิชาเกษตร

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

พ.ศ. 2537

ISBN 974-584-483-7

ลิขสิทธิ์ของบัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

PHYTOCHEMICAL STUDIES OF *XYRIS INDICA* LINN. FLOWERS

Pol. Lt. Suchada Sukrong

A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science in Pharmacy

Department of Pharmacognosy

Graduate School

Chulalongkorn University

1994

ISBN 974-584-483-7



Thesis Title      PHYTOCHEMICAL STUDIES OF *XYRIS INDICA* LINN. FLOWERS.  
By                      Pol. Lt. Suchada Sukrong  
Department        Pharmacognosy  
Thesis Advisor    Assistant Professor Thatree Phadungcharoen, M.Sc.

---

Accepted by the Graduate School, Chulalongkorn University in  
Partial Fulfillment of the Requirements for the Master's Degree.

.....*Thavorn Vajrabhaya*.....Dean of Graduate School  
(Professor Thavorn Vajrabhaya, Ph.D.)

Thesis committee :

.....*Chaiyo Chaichantipyuth*.....Chairman  
(Associate Professor Chaiyo Chaichantipyuth, M.Sc.)

.....*Thatree Phadungcharoen*.....Thesis Advisor  
(Assistant Professor Thatree Phadungcharoen, M.Sc.)

.....*Kalaya Pharadai*.....Member  
(Associate Professor Kalaya Pharadai, M.Eng.)

.....*Ekarin Saifah*.....Member  
(Associate Professor Ekarin Saifah, Ph.D.)



พิมพ์ต้นฉบับบทความวิจัยวิทยานิพนธ์ภายในกรอบสี่เหลี่ยมนี้เพียงแผ่นเดียว

สุชาติ สุธรอง, ร้อยตำรวจโทหญิง : การศึกษาทางพฤกษเคมีของดอกกระถินทุ่ง  
(PHYTOCHEMICAL STUDIES OF XYRIS INDICA LINN. FLOWERS) อ.ที่ปรึกษา  
: ผศ.ชาติ ผดุงเจริญ, 172 หน้า. ISBN 974-584-483-7

ได้ทำการแยกสารประกอบจากสิ่งสกัดคลอโรฟอร์มของช่อดอกกระถินทุ่ง Xyris indica Linn. (Xyridaceae) สามารถแยกสารกลุ่ม isocoumarin ชนิดใหม่ได้ 2 ชนิดคือ xyridin A และ B จากการศึกษาทางสเปกโตรสโคปีทำให้ทราบสูตรโครงสร้าง ซึ่งได้แก่ 3-n-propyl-6,7-(methylenedioxy)-1H-2-benzopyran-1-one และ 3-(1'-oxopropyl)-6,7-(methylenedioxy)-1H-2-benzopyran-1-one นอกจากนี้สามารถแยก chrysazin (1,8-dihydroxy-9,10-anthracenedione) และ 3-methoxy-chrysazin (1,8-dihydroxy-3-methoxy-9,10-anthracenedione) และสารชนิดใหม่ที่ยังไม่เคยมีรายงานว่าพบในที่ช่อดอกก่อนคือ 3-hydroxy-chrysazin (1,3,8-trihydroxy-9,10-anthracenedione) และสารพวกสเตอรอยด์ 2 ชนิดได้แก่  $\alpha$ -spinasterol และ stigmasterol พร้อมกันนี้ได้อภิปรายถึงชีวสังเคราะห์ของ xyridin A และ B อีกด้วย

ภาควิชา ..... เกษีชเวท  
สาขาวิชา ..... -  
ปีการศึกษา ..... 2536

ลายมือชื่อนิสิต ..... วิชา.ท.หญิง  
ลายมือชื่ออาจารย์ที่ปรึกษา ..... หน้ ผดุงเจริญ  
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม .....

## C475236 : MAJOR PHARMACOGNOSY  
KEY WORD: Xyris indica/ANTHRAQUINONE/ISOCOUMARIN/STEROID

SUCHADA SUKRONG, POLICE LIEUTENANT : PHYTOCHEMICAL STUDIES OF XYRIS INDICA LINN. FLOWERS. THESIS ADVISOR : ASSIS.PROF. THATREE PHADUNGCHAROEN, M.Sc.in Pharm. 172 pp. ISBN 974-584-483-7

Two new isocoumarins named xyridin A and B were isolated from the chloroform extract of the flowering heads of Xyris indica Linn.(Xyridaceae). Their structures have been established as 3-n-propyl-6,7-(methylenedioxy)-1H-2-benzopyran-1-one and 3-(1'-oxopropyl)-6,7-(methylenedioxy)-1H-2-benzopyran-1-one by means of spectroscopic analyses. Additionally, 3-hydroxy-chrysazin (1,3,8-trihydroxy-9,10-anthracenedione), a new plant constituent has been isolated along with chrysazin (1,8-dihydroxy-9,10-anthracenedione) and 3-methoxy-chrysazin (1,8-dihydroxy-3-methoxy-9,10-anthracenedione) and two known phytosterols,  $\alpha$ -spinasterol and stigmasterol. A possible biogenetic pathway for the formation of the xyridins has been proposed.

ภาควิชา..... เกษีชเวท  
สาขาวิชา..... -  
ปีการศึกษา..... 2536

ลายมือชื่อนิสิต..... ร.ท.ท.หญิง สักดิ์  
ลายมือชื่ออาจารย์ที่ปรึกษา..... นพ. อรุณศรี  
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..... -



## ACKNOWLEDGEMENTS

The author wishes to express her grateful appreciation to those who assisted her in the research as the following.

To Assistant Professor Thatree Phadungcharaon, her advisor, Department of Pharmacognosy, Faculty of Pharmaceutical Sciences, Chulalongkorn University, for her supervision of the research, ideas, keen interest, kindness, continual encouragement, and understanding during the course of practical work and presentation of the thesis.

To Associate Professor Nijsiri Ruangrunsi, Department of Pharmacognosy, Faculty of Pharmaceutical Sciences, Chulalongkorn University, for his helpful suggestion, innumerable assistant, and kindness throughout this research.

To Mr. Toshikazu Sekine, Research Associate, Department of Pharmacognosy, Faculty of Pharmaceutical Sciences, Chiba University, Japan, for his assistance in NMR experiments.

To all the pharmacists of the Department of Pharmacy, Police General Hospital for their encouragement throughout the research.

To all the staff members of the Department of Pharmacognosy, Faculty of Pharmaceutical Sciences, Chulalongkorn University, for their kindness and valuable helps.

To her parents for their love, warmth and understanding throughout her graduate study.

To Police Captain Smarn Sukrong, Police Department, for his encouragement and valuable helps throughout this research.

To the Graduate School of Chulalongkorn University for granting partial financial support (7,700 bahts).



## CONTENTS

	Page
ABSTRACT (Thai).....	iv
ABSTRACT (English).....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	viii
LIST OF FIGURES.....	x
LIST OF TABLES.....	xiv
ABBREVIATIONS.....	xv
CHAPTER I INTRODUCTION.....	1
CHAPTER II HISTORICAL.....	7
1. ANTHRAQUINONES.....	7
1.1 DISTRIBUTION OF ANTHRAQUINONES.....	7
1.2 CHEMISTRY OF ANTHRAQUINONES.....	9
1.3 CLASSIFICATION OF ANTHRAQUINONES.....	14
1.4 BIOSYNTHESIS OF ANTHRAQUINONES.....	16
2. STEROIDS.....	24
2.1 DISTRIBUTION OF STEROIDS.....	24
2.2 CHEMISTRY OF STEROIDS.....	26
2.3 CLASSIFICATION OF STEROIDS.....	28
2.4 BIOSYNTHESIS OF PLANT STEROLS.....	44
3. ISOCOUMARINS.....	49
3.1 DISTRIBUTION OF ISOCOUMARINS.....	49
3.2 CHEMISTRY OF ISOCOUMARINS.....	57
3.3 BIOSYNTHESIS OF ISOCOUMARINS.....	57

	Page
CHAPTER III EXPERIMENTAL.....	60
1. SOURCE OF PLANT MATERIAL.....	60
2. GENERAL TECHNIQUES.....	60
3. EXTRACTION AND ISOLATION.....	64
4. IDENTIFICATION OF ISOLATED COMPOUNDS.....	66
CHAPTER IV DISCUSSION.....	87
CHAPTER V CONCLUSION AND RECOMMENDATION.....	106
• REFERENCES.....	108
APPENDIX.....	114
VITA.....	172

## LIST OF FIGURES

Figure		Page
1	กระต๊อ <i>Xyris indica</i> Linn. (Drawing).....	5
2	กระต๊อ <i>Xyris indica</i> Linn. (Photograph).....	6
3	Acetate-malonate pathway of anthraquinones.....	18
4	Shikimate-mevalonate pathway of anthraquinones.....	20
5	Migration of radioactivity from different precursors to morindone.....	23
6	Squalene biosynthesis.....	47
7	Biosynthetic pathway of plant sterol.....	48
8	Alternative possible folding for cyclization of the C-8 polyketide relation to the position of the [1,2- <sup>13</sup> C <sub>2</sub> ] acetate units.....	58
9	Possible cyclization sequence of the C-8 polyketide leading to 2,4-dihydroxyacetophenone as defined by the observed connectivity of the [1,2- <sup>13</sup> C <sub>2</sub> ] acetate units..	59
10	Incorporation of [1,2- <sup>13</sup> C <sub>2</sub> ] acetate into mellein.....	59
11-15	Thin layer chromatograms of isolated compounds.....	115-119
16	Ultraviolet absorption spectrum of XI-1.....	120
17	Infrared absorption spectrum of XI-1.....	121
18	<sup>1</sup> H-NMR spectrum of XI-1.....	122
19	Expansion of <sup>1</sup> H-NMR spectrum of XI-1.....	123
20	<sup>13</sup> C-NMR spectrum of XI-1.....	124
21	EI mass spectrum of XI-1.....	125
22	Ultraviolet absorption spectrum of XI-2.....	126
23	Infrared absorption spectrum of XI-2.....	127

	Page
24	$^1\text{H}$ -NMR spectrum of XI-2..... 128
25	Expansion of $^1\text{H}$ -NMR spectrum of XI-2..... 129
26	EI mass spectrum of XI-2..... 130
27	Ultraviolet absorption spectrum of XI-3..... 131
28	Infrared absorption spectrum of XI-3..... 132
29	$^1\text{H}$ -NMR spectrum of XI-3..... 133
30	Expansion of $^1\text{H}$ -NMR spectrum of XI-3..... 134
31	$^{13}\text{C}$ -NMR spectrum of XI-3..... 135
32	$^{13}\text{C}$ -NMR spectrum of XI-3 (DEPT)..... 136
33	$^{13}\text{C}$ - $^1\text{H}$ COSY spectrum of XI-3 ..... 137
34	HMBC spectrum of XI-3..... 138
35	Expansion of HMBC spectrum of XI-3..... 139
36	HREI mass spectrum of XI-3..... 140
37	Infrared absorption spectrum of XI-4..... 141
38	$^1\text{H}$ -NMR spectrum of XI-4..... 142
39	Expansion of $^1\text{H}$ -NMR spectrum of XI-4..... 143
40	$^{13}\text{C}$ -NMR spectrum of XI-4..... 144
41	Expansion of $^{13}\text{C}$ -NMR spectrum of XI-4..... 145
42	EI mass spectrum of XI-4..... 146
43	Infrared absorption spectrum of XI-5..... 147
44	$^1\text{H}$ -NMR spectrum of XI-5..... 148
45	Expansion of $^1\text{H}$ -NMR spectrum of XI-5..... 149
46	$^{13}\text{C}$ -NMR spectrum of XI-5..... 150
47	Expansion of $^{13}\text{C}$ -NMR spectrum of XI-5..... 151
48	EI mass spectrum of XI-5..... 152
49	Ultraviolet absorption spectrum of XI-6..... 153

	Page
50	Infrared absorption spectrum of XI-6..... 154
51	$^1\text{H}$ -NMR spectrum of XI-6..... 155
52	Expansion of $^1\text{H}$ -NMR spectrum of XI-6..... 156
53	$^{13}\text{C}$ -NMR spectrum of XI-6..... 157
54	$^{13}\text{C}$ -NMR spectrum of XI-6 (DEPT)..... 158
55	$^{13}\text{C}$ - $^1\text{H}$ COSY spectrum of XI-6 ..... 159
56	HMBC spectrum of XI-6..... 160
57	Expansion of HMBC spectrum of XI-6..... 161
58	HREI mass spectrum of XI-6..... 162
59	Ultraviolet absorption spectrum of XI-7..... 163
60	Infrared absorption spectrum of XI-7..... 164
61	$^1\text{H}$ -NMR spectrum of XI-7..... 165
62	Expansion of $^1\text{H}$ -NMR spectrum of XI-7..... 166
63	$^{13}\text{C}$ -NMR spectrum of XI-7..... 167
64	$^{13}\text{C}$ -NMR spectrum of XI-7 (DEPT)..... 168
65	HMBC spectrum of XI-7..... 169
66	Expansion of HMBC spectrum of XI-7..... 170
67	HREI mass spectrum of XI-7..... 171
68	The C-H correlations observed from HMBC spectrum of XI-7..... 92
69	The proposed fragmentation patterns of XI-1, XI-2 and XI-7 from EI mass spectrum..... 92
70	The proposed fragmentation patterns of XI-4..... 96
71	The proposed fragmentation patterns of XI-5..... 98
72	The C-H correlations observed from HMBC spectrum of XI-3..... 100

	Page
73 The proposed fragmentation patterns of XI-3.....	101
74 The C-H correlations observed from HMBC spectrum of XI-6.....	103
75 The proposed fragmentation patterns of XI-6.....	104
76 Hexaketide for the formation of skeleton of the xyridins..	105
77 Heptaketide for the formation of skeleton of the xyris anthraquinones.....	105

## LIST OF TABLES

Table		Page
1.	Occurrence of some animal steroid hormones in plants.....	37
2.	Carbon and proton assignments of XI-7 and long-range correlations between carbon and proton by HMBC spectrum...	93
3.	Carbon and proton assignments of XI-3 and long-range correlations between carbon and proton by HMBC spectrum...	101
4.	Carbon and proton assignments of XI-6 and long-range correlations between carbon and proton by HMBC spectrum...	104

## ABBREVIATIONS

$\epsilon$ max	=	Molar absorptivity at maximum absorption
br	=	Broad (for NMR spectra)
$^{\circ}\text{C}$	=	Degree Celcius
$^{13}\text{C-NMR}$	=	Carbon-13 Nuclear Magnetic Resonance
cm	=	Centimeter
d	=	Doublet (for NMR spectra)
dd	=	Doublets of doublet (for NMR spectra)
DEPT	=	Distortionless Enhancement by Polarization Transfer
dq	=	Double of quartet (for NMR spectra)
DMSO- $d_6$	=	Dimethyl sulfoxide- $d_6$
$\delta$	=	Chemical shift
EIMS	=	Electron Impact Mass Spectrum
eV	=	Electron volt
g	=	Gram
HMBC	=	Heteronuclear Multiple Bond Connectivity
HREIMS	=	High Resolution Electron Impact Mass Spectrum
Hz	=	Hertz
$^1\text{H-NMR}$	=	Proton Nuclear Magnetic Resonance
IR	=	Infrared
KBr	=	Potassium bromide
kg	=	Kilogram
L	=	Liter
m	=	Meter

m	=	Multiplet (for NMR spectra)
M <sup>+</sup>	=	Molecular ion
λ max	=	Wavelength at maximum absorption
m/z	=	Mass to charge ratio
mg	=	Milligram
MHz	=	Mega Hertz
ml	=	Milliliter
mm	=	Millimeter
m.p.	=	Melting point
MS	=	Mass Spectrum
nm	=	Nanometer
NMR	=	Nuclear Magnetic Resonance
ppm	=	Part per million
q	=	Quartet (for NMR spectra)
s	=	Singlet (for NMR spectra)
t	=	Triplet (for NMR spectra)
TLC	=	Thin layer chromatography
UV	=	Ultraviolet