Chemical Constituents from the Latex of *Garcinia cowa* and Antioxidation Properties

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Master of Science Thesis in Organic Chemistry

Prince of Songkla University

2001

Thesis Title	Chemical Constituents from the Latex of *Garcinia cowa* and Antioxidation Properties
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Major Program	Organic Chemistry

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The Graduate School, Prince of Songkla University, has approved this thesis as partial fulfillment of the requirement for the Master of Science Degree in Organic Chemistry.

....

(Piti Trisdikoon, Ph. D.)

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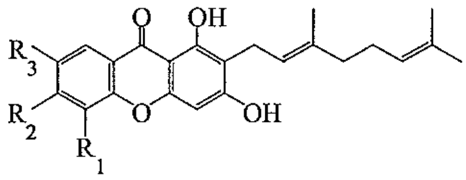
ชื่อวิทยานิพนธ์	องค์ประกอบทางเคมีจากน้ำยางชะมวง (*Garcinia cowa*) และสมบัติต้านปฏิกิริยาออกซิเดชัน
ผู้เขียน	นางสาวปริชาติ ไชยฤกษ์
สาขาวิชา	เคมีอินทรีย์
ปีการศึกษา	2544

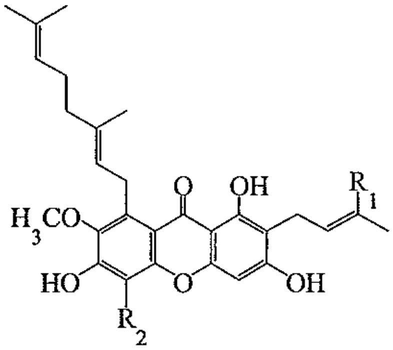
บทคัดย่อ

การแยกสารองค์ประกอบจากน้ำยางชะมวง (*Garcinia cowa* Roxb.) โดยวิธีการทางโครมาโทกราฟีและการตกผลึก สามารถแยกสารประเภทแซนโทน (xanthones) ซึ่งเป็นสารใหม่ 7 สาร ได้แก่ 5,9-dihydroxy-8-methoxy-2,2-dimethyl-7-(3,7-dimethyl-2,6-octadienyl)-*2H,6H*-pyrano[3,2-*b*]xanthen-6-one (**PGC6**), 1,3,6-trihydroxy-7-methoxy-2,5-bis(3-methyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl)xanthone (**PGC7**), 1,6-dihydroxy-3,7-dimethoxy-2-(3-methyl-2-butenyl)xanthone (**PGC8**), 1,6-dihydroxy-3,5-dimethoxy-2-(3-methyl-2-butenyl)xanthone (**PGC9**), 1,6-dihydroxy-3,7-dimethoxy-2-(4-hydroxy-3-methyl-2-butenyl)xanthone (**PGC10**), 6,8,12-trihydroxy-7-(3-methyl-2-butenyl)-2-methyl-2-(4-methyl-3-pentenyl)pyrano(2′,3′:7,8)xanthone (**PGC11**) และ 1,3,6-trihydroxy-7-methoxy-2-(3-methyl-4-*O*-acetyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl)xanthone (**PGC12**) และสารที่เคยมีรายงานแล้ว 5 สาร ได้แก่ cowaxanthone (**PGC1**), cowanin (**PGC2**), cowanol (**PGC3**), 1,3,6-trihydroxy-7-methoxy-2,5-bis(3-methyl-2-butenyl)xanthone (**PGC4**) และ mangostinone (**PGC5**) โครงสร้างของสารเหล่านี้วิเคราะห์โดยใช้ข้อมูลทางสเปกโทรสโกปี UV IR และ NMR

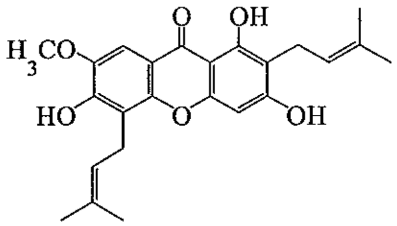
น้ำยางชะมวงและสารบริสุทธิ์ **PGC1, PGC2, PGC3, PGC4, PGC6, PGC7** และ **PGC12** เมื่อนำมาทดสอบฤทธิ์ต้านปฏิกิริยาออกซิเดชันเบื้องต้นด้วย α,α-diphenyl-β-picrylhydrazyl radical พบว่าน้ำยางแสดงฤทธิ์ต้านปฏิกิริยาออกซิเดชันได้ดีด้วยค่า IC_{50} 13.20 μg/ml ในขณะที่สารบริสุทธิ์แสดงฤทธิ์ต้านปฏิกิริยาออกซิเดชันได้เล็กน้อย



	R_1	R_2	R_3
PGC1 :	H	OH	OCH_3
PGC5 :	OH	H	H



	R_1	R_2
PGC2 :	CH_3	H
PGC3 :	CH_2OH	H
PGC7 :	CH_3	isoprenyl
PGC12 :	CH_2OAc	H



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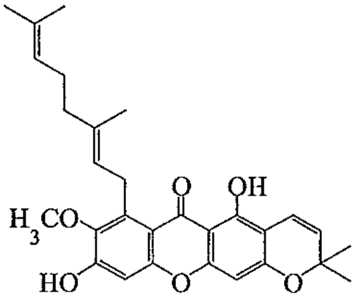

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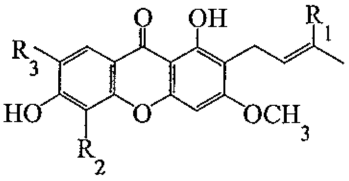
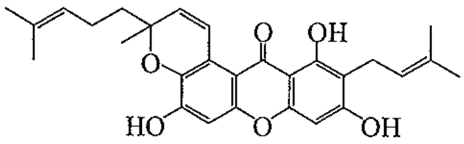


		R_1	R_2	R_3
PGC8	:	CH_3	H	OCH_3
PGC9	:	CH_3	OCH_3	H
PGC10	:	CH_2OH	H	OCH_3



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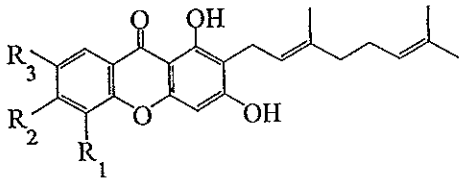
Thesis Title	Chemical Constituents from the Latex of *Garcinia cowa* and Antioxidation Properties
Author	Miss Parichat Chairerk
Major Program	Organic Chemistry
Academic Year	2001

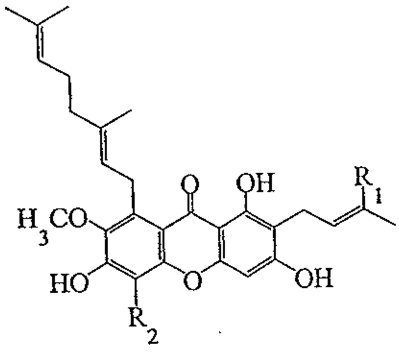
Abstract

Isolation of the chemical constituents from the latex of *Garcinia cowa* Roxb., by chromatographic and crystallization technique, yielded seven new xanthones: 5,9-dihydroxy-8-methoxy-2,2-dimethyl-7-(3,7-dimethyl-2,6-octadienyl)-*2H,6H*-pyrano[3,2-*b*]xanthen-6-one **(PGC6)**, 1,3,6-trihydroxy-7-methoxy-2,5-bis(3-methyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl)xanthone **(PGC7)**, 1,6-dihydroxy-3,7-dimethoxy-2-(3-methyl-2-butenyl)xanthone **(PGC8)**, 1,6-dihydroxy-3,5-dimethoxy-2-(3-methyl-2-butenyl)xanthone **(PGC9)**, 1,6-dihydroxy-3,7-dimethoxy-2-(4-hydroxy-3-methyl-2-butenyl)xanthone **(PGC10)**, 6,8,12-trihydroxy-7-(3-methyl-2-butenyl)-2-methyl-2-(4-methyl-3-pentenyl)pyrano(2′,3′:7,8)xanthone **(PGC11)** and 1,3,6-trihydroxy-7-methoxy-2-(3-methyl-4-*O*-acetyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl)xanthone **(PGC12)** and five previously reported xanthones: cowaxanthone **(PGC1)**, cowanin **(PGC2)**, cowanol **(PGC3)**, 1,3,6 trihydroxy-7-methoxy-2,5-bis(3-methyl-2-butenyl)xanthone **(PGC4)** and mangostinone **(PGC5)**. Their structures were elucidated on the basis of UV, IR and NMR spectroscopic data.

The crude material and its pure compounds **PGC1, PGC2, PGC3, PGC4, PGC6, PGC7** and **PGC12** were examined for their antioxidative activity by a *α,α*-diphenyl-*β*-picrylhydrazyl (DPPH) free radical scavenging assay. The crude material exhibited strong activity with IC_{50} 13.20 μg/ml, whereas the pure compounds showed very weak activity.



	R_1	R_2	R_3
PGC1 :	H	OH	OCH_3
PGC5 :	OH	H	H



	R_1	R_2
PGC2 :	CH_3	H
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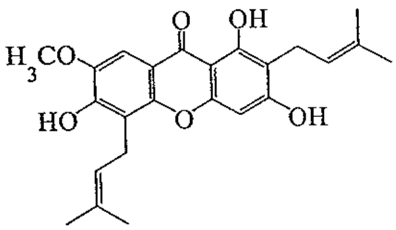
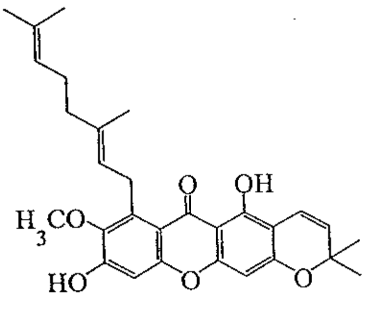
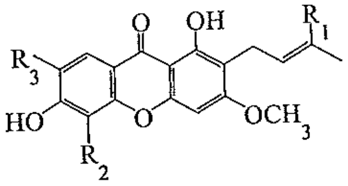
PGC7 :	CH_3	isoprenyl
PGC12 :	CH_2OAc	H



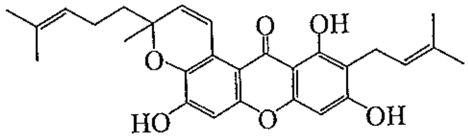
PGC4



PGC6



	R_1	R_2	R_3
PGC8 :	CH_3	H	OCH_3
PGC9 :	CH_3	OCH_3	H
PGC10 :	CH_2OH	H	OCH_3



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I would also like to express my appreciation to the staffs of the Department of Chemistry, Faculty of Science, Prince of Songkla University for making this thesis possible and to Ms. Dusanee Langjae, the Scientific Equipment Center, Prince of Songkla University for recording the 500 MHz NMR spectra.

Finally, none of this would have been possible without love and encouragement of my family and friends. I thank them all for their kindness and valuable advice. Everything will always keep in my mind.

Parichat Chairerk

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ABBREVIATIONS AND SYMBOLS

s = *singlet*

d = *doublet*

t = *triplet*

m = *multiplet*

br s = *broad singlet*

br t = *broad triplet*

dd = *doublet of doublet*

dt = *doublet of triplet*

δ = chemical shift relative to TMS

J = coupling constant

Hz = hertz

MHz = megahertz

ppm = part per million

m.p. = melting point

R_f = retention factor

g = gram

mg = milligram

μg = microgram

mM = millimolar

ml = milliliter

μl = microliter

% = percentage

min = minute

ABBREVIATIONS AND SYMBOLS (Continued)

c = concentration

ε = molar extinction coefficient

λ_{max} = maximum wavelengh

nm = nanometer

ν = absorption frequencies

cm^{-1} = resiprocal centimeter (wavenumber)

°C = degree celcius

DEPT = Distortionless Enhancement by Polarization Transfer

FTIR = Fourier Transform Infrared

HMBC = Heteronuclear Multiple Bond Correlation

HMQC = Heteronuclear Multiple Quantum Coherence

IR = Infrared

^{1}H NMR = Proton Nuclear Magnetic Resonance

^{13}C NMR = Carbon Nuclear Magnetic Resonance

2D NMR = Two Dimentional Nuclear Magnetic Resonance

NOE = Nuclear Overhauser Effect

PLC = Preparative Thin-layer Chromatography

TLC = Thin-layer Chromatography

UV = Ultraviolet

CD_3COCD_3 = deuteroacetone

DMSO = dimethylsulphoxide

TMS = tetramethylsilane

ABBREVIATIONS AND SYMBOLS (Continued)

$CDCl_3$ = deuterochloroform

CD_3OD = deuteromethanol

D_2O = deuterium oxide

IC_{50} = 50% Inhibition Concentration

DPPH = α,α-diphenyl-β-picrylhydrazyl radical

CHAPTER 1

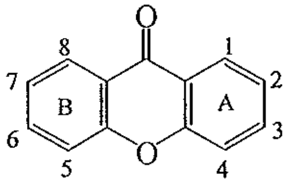
INTRODUCTION

1.1 Introduction

Garcinia cowa Roxb. known as the Cha-muang tree, belongs to the Guttiferae family. It grows widely in the tropical rain forest area. The family Guttiferae contains about 40 genera and over 1000 species. Only 6 genera and 60 species are found in Thailand; i.e., *Calophyllum, Cratoxylum, Garcinia, Kayea* and *Orchrocarpus* (Roulean, 1981). *G. cowa* is an erect small to medium tree, reaching 60 feet tall. The trunk is simple straight, the branches are slender and lower reaching the ground. It has dark-gray bark, inner bark with opaque, lemon yellow exudate. The leaves are broad-lanceolate acute at both ends dark green beneath 3-5 by 1-2 inches size, the veins are 0.1-0.15 inches apart, its slender, regular and inarching with an intra-marginal one, drying pinkish grey-brown, the young leaves are red and edible. Male flowers are in 3-8 flowered which rarely auxillary umbels, male pedicels are 0.16-0.33 inches, sepals are 0.16 inches in length, broad-ovate, with a thick fleshy, the colour of sepal is yellow and pink on both surfaces. Petals twice as long as with sepals and oblong. Stamens numerous forming a quadrate mass, with a rudimentary stigma O, anthers in a shortly subsessile, 4-celled. Hermaphroditic flower is solitary which rarely 2-3 at axillary and sessile. Ovary is subglobose, with stigmatic rays spreading and papillose. Stamens (sterile) in 4 clusters of 3-8 unequal filaments. Fruit have orange or dark-yellow of small size, drying jet black, with 4-8 grooved to the top with a tip mamilla (Hooker, 1875). Seeds embedded in pale orange pulp.

1.2 Review of Literatures

The study of xanthones is interesting not only for the chemosystematic investigation but also from the pharmacological point of view. Since the structures of the most xanthones are phenolic compounds that have free hydroxy groups on the xanthone nucleus and usually show various biological activities. The various bioactivities of xanthones that have been described include cytotoxic and antitumor activity, anti-inflammatory activity, antifungal activity and inhibition of lipid peroxidase (Iinuma, 1994). Xanthones are secondary metabolites commonly occurring in a few higher plant families, fungi and lichens. The symmetrical nature of the xanthone nucleus, coupled with its mixed biogenetic origin in higher plants necessitates that the carbons be numbered according to a biosynthetic convention. Carbons 1-4 are assigned to the acetate-derived ring A, and carbons 5-8 to the shikimate-derived ring B (Bennett and Lee, 1989).



Xanthone basic skeleton

The large genus *Garcinia*, which is mainly encountered in lowland rainforests of the tropical world and are found from sea level to the tops of the highest mountains, has been classified into the Guttiferae family. The plants in the *Garcinia* genus are well known to be rich in a variety of oxygenated and prenylated xanthones (Bennett and Lee, 1989).

Xanthones isolated from 44 species of the *Garcinia* genus were summarized in Table 1.

Table 1 Xanthones from plants of the *Garcinia* genus

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. assigu Lantb. (stem bark)	1,5-di(OH)xanthone	1	Ito, *et al.*, 1997
	assiguxanthone A, B	2, 3	
	1,3,6,7-tetra(OH)-8-(3-(Me)but-2-enyl)xanthone	4	
	toxyloxanthone B	5	Ito, *et al.*, 1998
	1,3,5-tri(OH)xanthone	6	
	pancixanthone A	7	
G. atroviridis (stem bark)	atroviridin	8	Kosin, *et al.*, 1998
G. bracteata (leaves)	bractatin	9	Thoison, *et al.*, 2000
	1-*O*-methylbractatin	10	
	isobractatin	11	
	1-*O*-methylisobractatin	12	
	1-*O*-methylneobractatin	13	
	1-*O*-(Me)-8-(OMe)-8,8a-dihydrobractatin	14	

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. buchananii			
(heartwood)	1,5-di(OH)xanthone	1	Jackson, *et al.*,
	1,5,6-tri(OH)xanthone	15	1968
	buchanaxanthone	16	
G. cambogia			
(root)	garbogiol	17	Iinuma, *et al.*,
(bark)	rheediaxanthone A	18	1998
G. cowa Roxb.			
(latex)	cowanin	19	Na Pattalung, *et*
	cowanol	20	*al.*, 1994
	cowaxanthone	21	
	1,3,6-tri(OH)-7-(OMe)-2,5-bis (3-(Me)-2-butenyl)xanthone	22	
	norcowanin	25	
(stem)	cowanin	19	Krahn, 1968
	cowanol	20	
	cowaxanthone	21	
	1,3,6-tri(OH)-7-(OMe)-8-(3,7-di (Me)-2,6-octadienyl)xanthone	23	Lee and Chan, 1977

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. cowa Roxb. (stem bark)	7-*O*-methylgarcinone E	24	Likhitwitayawuid, *et al.*, 1997
	β-mangostin cowanin cowanol cowaxanthone	26 19 20 21	Likhitwitayawuid, *et al.*, 1998a
G. densivenia (stem bark)	pyranojacareubin	27	Waterman and Crichton, 1980a
	rheediaxanthone A	18	Bennett and Lee, 1989
G. dioica (bark)	1,3,7-tri(OH)-2,4-diisoprenyl-xanthone 1,3,6-tri(OH)-8-(7-(OH)-3,7-di-(Me)-2,5-octadienyl)-7-(OMe)-xanthone 1,3,6-tri(OH)-8-(6,7-epoxy-3,7-di-(Me)-2-octenyl)-7-(OMe) xanthone	28 29 30	Iinuma, *et al.*, 1996b

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. dioica			
(bark)	rubraxanthone	23	Iinuma, *et al.*, 1996b
G. dulcis			
(bark)	symphoxanthone	31	Likhitwitayawuid, *et al.*, 1998b
	1-*O*-methylsymphoxanthone	32	
	1,7-di(OH)xanthone	33	
	garciniaxanthone	34	
	12b-(OH)-des-D-garcigerrin A	38	
(branches)	1,4,6-tri(OH)-5-(OMe)-7-(3-(Me)but-2-enyl)xanthone	41	Harrison, *et al.*, 1994
(leaves)	dulxanthone E	43	Kosela, *et al.*, 1999
G. dulcis			
(leaves)	dulxanthone F-H	44-46	Kosela, *et al.*, 2000
(root)	garciduol A-C	47-49	Iinuma, *et al.*, 1996a, c
	1,3,6-tri(OH)-7-(OMe)xanthone	35	
	1,3,6-tri(OH)-8-isoprenyl-7-(OMe) xanthone	36	
	1,3,6-tri(OH)-5-(OMe) xanthone	37	
	1,3,5-tri(OH) xanthone	6	

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. dulcis			
(root)	1,4,5-tri(OH) xanthone	42	Iinuma, *et al.*, 1996a, c
	2,5-di(OH)-1-(OMe)xanthone	50	
	dulciol B-E	51-54	Iinuma, *et al.*, 1996d
	garciniaxanthone A	39	
	garciniaxanthone B, D	55,56	
	subelliptenone C, D	59,60	
	subelliptenone F	40	
	globuxanthone	57	
	12b-(OH)-des-D-garcigerin	38	
	dulciol B-D	51-53	Harrison, *et al.*, 1994
	dulciol A	61	Iinuma, *et al.*, 1996d
	12b-(OH)-des-D-garcigerrin	38	
	toxyloxanthone B	6	
(stem bark)			
	dulxanthone A-D	64-67	Ito, *et al.*, 1997, 1998
	gentisein	68	
	1,3,7-tri(OH)-2-(3-methylbut-2-enyl)xanthone	69	

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. dulcis (stem bark)	ugaxanthone	70	Ito, *et al.*, 1997, 1998
	isoprenylxanthone	71	
	jacareubin	72	
	xanthone VI	73	
G. echinocarpa (bark)	1,3,6,7-tetra(OH)xanthone	62	Bandaranayake, *et al.*, 1975
(wood)	1,5-di(OH)xanthone	1	
G. eugeniifolia (heartwood)	gentisin	74	Jackson, *et al.*, 1969
	1,4,7-tri(OH)-3-(OMe)-xanthone	75	
	1,6,7-tri(OH)xanthone	76	
	euxanthone	33	
	1,5,6-tri(OH)xanthone	15	
G. forbesii (branches and stem)	forbexanthone	77	Harrison, *et al.*, 1993
	1,3,7-tri(OH)-2-(3-(Me)but-2-enyl)xanthone	69	
	pyranojacareubin	27	
	forbesione	78	Leong, *et al.*, 1996

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. gaudichaudii			
(leaves)	gaudichaudione A-D	79-82	Cao, *et al.*, 1998a
	gaudichaudione E-H	83-85	Cao, *et al.*, 1998b
	gaudichaudiic acid A-E	87-90	
	morellic acid	92	
	forbesione	78	Wu, *et al.*, 2000
	gaudichaudione I	-	
	gaudichaudione J	-	
(stem bark)	gaudichaudiic acid F-I	93-96	Xu, *et al.*, 2000
	gaudichaudiic acid E	91	Wu, *et al.*, 2001
	morellic acid	92	
	gaudispirolactone	97	
	7-isoprenylmorellic acid	98	
	isomoreollin	99	
	isomorellinol	100	
	isomorellin	101	
	isomorellic acid	102	
G. gerrardii			
(root bark)	garcigerrin A	103	Sordat-Diserens, *et al.*, 1989
	garcigerrin B	104	
	12b-(OH)-des-D-garcigerrin A	38	

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G.griffithii (bark)	griffipavixanthone	105	Xu, *et al.*, 1998
G. hanburyi (latex)	gambogic acid	106	Lu, *et al.*, 1984,
	neogambogic acid	-	Lu and Fang, 1988
	isogambogic acid	107	Lin, *et al.*, 1993
	isomorellinol	100	
	morellic acid	92	Asano, *et al.*, 1996
	isomorellin	101	
	gambogic acid	106	
	gambogin	108	
	gambogenin	109	
	isogambogenin	110	
	gambogenic acid	111	
	desoxygambogenin	112	
	gambogenin dimethyl acetal	113	
	desoxymorellin	114	
	morellin dimethyl acetal	115	
(stem bark)	isomoreollin B	116	
	moreollic acid	117	
	hanburin	118	
	gambogellic acid	119	

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. indica (heartwood)	euxanthone	33	Cotterill, *et al.*, 1977
G. kola Heckel (stem)	1,5-di(OH)xanthone 2,5-di(OH)-1-(OMe)xanthone 2-(OH)xanthone 4-(OH)xanthone 3-(OH)-4-(OMe)xanthone 2-(OH)-1-(OMe)xanthone 2-(OH)-1,8-di(OMe)xanthone 1,2-di(OMe)xanthone 1,2,8-tri(OMe)xanthone 1,3,5-tri(OH)-2-(OMe)xanthone	1 50 120 121 122 123 124 125 126 127	Terashima, *et al.*, 1999
G. latissima (stem bark)	latisxanthone A-D pyranojacareubin	132-135 27	Ito, *et al.*, 1997 Ito, *et al.*, 1998
G. livingstonei (root bark)	12b-(OH)-des-D-garcigerrin A 1,4,5-tri(OH)-3-(3-(Me)but-2-enyl)-9H-xanthen-9-one	38 128	Sordat-Diserens, *et al.*, 1992a

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. livingstonei			
(root bark)	1,3,5-tri(OH)-4-(3′,7′-di(Me) octa-2′,6′-dienyl)-9H-xanthen-9-one	129	Sordat-Diserens, *et al.*, 1992a
	6,11-di(OH)-2,2-di(Me)pyrano-[3,2-*c*]-xanthen-7(2H)-one	136	
	6,11-di(OH)-3-(Me)-3-(4-(Me) pent-3-enyl)-3H,7H-pyrano [2,3-*c*]-xanthen-7-one	137	
	garcilivin A-C	138-140	Sordat-Diserens, *et al.*, 1992b
G. mangostana			
(aril)	mangostin	141	Mahabusarakam, *et al.*, 1987
	calabaxanthone	143	
	demethylcalabaxanthone	144	
	1,3,7-tri(OH)-2,8-bis-(γ,γ-di (Me)allyl)xanthone	145	
	1,7-di(OH)-3-(OMe)-2-(γ,γ-di (Me)allyl)xanthone	146	
(bark)	mangostin	141	Yates, *et al.*, 1958; Jefferson, *et al.*, 1970
	β-mangostin	26	

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
(fruit hull)	mangostin (α-mangostin)	141	Yates and Stout, 1958; Sen, *et al.*, 1981
	normangostin	142	Jefferson, *et al.*, 1970
	gartanin	161	Govindachari, *et al.*, 1971
	8-desoxygartanin	162	
	5,9-di(OH)-8-(OMe)-2,2-di-Me -7-(3-(Me)but-2-enyl)-2H,6H -pyrano[3,2-*b*]xanthen-6-one	147	Sen, *et al.*, 1980
	1,7-di(OH)-2-(3-methylbut-2-enyl)-3-(OMe)-xanthone	146	Sen, *et al.*, 1981
	1,5-di(OH)-2-(3-methylbut-2-enyl)-3-(OMe)-xanthone	148	
	garcinone A-C	149-151	Sen, *et al.*, 1982
	β-mangostin	26	Mahabusarakam, *et al.*, 1984
	γ-mangostin	154	
	garcinone D	152	Sen, *et al.*, 1986
	1-isomangostin	157	Mahabusarakam, *et al.*, 1987
	1-isomangostin hydrate	158	
	3-isomangostin	159	
	3-isomangostin hydrate	160	

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. mangostana			
(fruit hulls)	BR-xanthone A	164	Balasubramanian and Rajagopalan, 1988
	BR-xanthone B	165	
	garcinone E	155	Sakai, *et al.*, 1993
	1,5,8-tri(OH)-3-(OMe)-2-(3-(Me)but-2-enyl)xanthone	163	
	6-desoxy-γ-mangostin	154	Asai, *et al.*, 1995
	mangostinone	130	Chairungsrilerd, *et al.*, 1996
	mangostanol	169	
	2,7-di-(3-(Me)but-2-enyl)-1,3,8-tri(OH)-4-(Me)xanthone	166	Gopalakrishnan, *et al.*, 2000
	2,8-di-(3-(Me)but-2-enyl)-7-carboxy-1,3-di(OH)xanthone	167	
	garcimangosone A		Huang, *et al*, 2001
	garcimangosone B		
	garcimangosone C		
(latex)	mangostin	141	Govindachari, *et al.*, 1971; Idris, *et al.*, 1977
	β-mangostin	26	
	γ-mangostin	145	
	gartanin	161	
	8-desoxygartanin	162	

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
(leaves)	gartanin	161	Perveen and Khan, 1988
	1,5,8-tri(OH)-3-(OMe)-2(3-(Me)-2-butenyl)xanthone	163	
	1,6-di(OH)-3-(OMe)-2(3-(Me)-2-butenyl)xanthone	168	
(ripe fruit)	mangostin	141	Govindachari, *et al.*, 1971
	β-mangostin	26	
(very ripe fruit)	mangostin	141	Govindachari, *et al.*, 1971
	γ-mangostin	145	
	gartanin	161	
	8-desoxygartanin	162	
(wood)	1,3,6,7-tetra(OH)xanthone	62	Holloway and Scheinmann, 1975
	glycoside of 1,3,6,7-tetra(OH) xanthone	63	
	BR-xanthone B	165	Balasubramaniam and Rajagopalan, 1988
	mangostinone	130	Asai, *et al.*, 1995

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. morella			
(hull)	moreollin	174	Subba Rao, *et al.*, 1987
(latex)	gambogic acid	106	Karanjgaokar, *et al.*, 1966
	morellic acid	92	
	isomoreollic acid	177	
(seed)	morellin	178	Bringi, *et al.*, 1955
	dihydroisomorellin	179	Bhat, *et al.*,1964
	ethoxydihydroisomorellin	174	
	deoxymorellin	114	
	isomoreollin	99	Nair and Venkataraman, 1964
(seed hulls)	moreollin	174	Rao, *et al.*, 1978
(trunk bark)	isomorellic acid	102	Adawadkar, *et al.*, 1976
G. multiflora			
(heartwood)	1,3,6,7-tetra(OH)xanthone	62	Chen, *et al.*, 1975
G. nervosa Miq.			
(stem bark)	nervosaxanthone	170	Ampofo and Waterman, 1986
	rubraxanthone	23	

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. opaca			
(leaves)	nervosaxanthone	170	Ampofo and Waterman, 1986
	macluraxanthone	181	Goh, *et al.*, 1992
	1,3,5-tri(OH)-6′,6′-di(Me)pyrano (2′,3′:6,7)-4-(1,1-di(Me)prop-2- enyl)-xanthone	175	
	1,3,5-tri(OH)-6′,6′-di(Me)pyrano (2′,3′:6,7)-2-(3-methylbut-2-enyl)-4-(1,1-di(Me)prop-2-enyl)xanthone	176	
	4″,5″-dihydro-1,5-di(OH)-6′,6′-di(Me)pyrano(2′,3′:6,7)-2-(3-(Me)but-2-enyl)-4″,4″,5″-tri(Me)furano(2″,3″:3,4) xanthone	180	
G. ovalifolia			
(stem bark)	macluraxanthone	181	Waterman and Crichton, 1980b

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. parvifolia			
(bark)	griffipavixanthone	105	Xu, *et al.*, 1998
(latex)	rubraxanthone	23	Na Pattalung, *et al.*, 1988
G. pedunculata			
(heartwood)	1,3,6,7-tetra(OH)xanthone	62	Rao, *et al.*, 1974
	1,3,5,7-tetra(OH)xanthone	182	
G. polyantha			
(stem bark)	isorheediaxanthone B	183	Ampofo and Waterman, 1986
G. puat Guillaumin			
(leaves)	1,3,7-tri(OH)-2-(2-butenyl-3-(Me))-xanthone	9	Ito, *et al.*, 2001
G.pyrifera			
(stem bark)	rubraxanthone	23	Ampofo and Waterman, 1986
	isocowanin	188	
	isocowanol	189	
G. quadrifaria			
(stem bark)	1,3,5-tri(OH)-4,8-bis(3′,3′-di-(Me)allyl)xanthone	184	Waterman and Hussain, 1982

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. schomburgkiana (root)	3-*O*-methylgarcinone B 1,3,7-tri(OH)-2,5,8-tris(3-(Me) but-2-enyl)-6-(OMe)xanthone	153 156	Na Pattalung, *et al.*, 1984
G. scortechinii (twigs)	scortechinone A-C	185-187	Rukachaisirikul, *et al.*, 2000
G. sessilis (heartwood)	5,9-di(OH)-8-(OMe)-2,2-di (Me)-7-(3-methylbut-2-enyl)-2*H*,6*H*-pyrano[3,2-*b*]xanthen-6-one	147	Ali, *et al.*, 1999
G. speciosa (bark)	cowanin cowanol α-mangostin	19 20 141	Okudaira, *et al.*, 2000
(leaves)	5,9,10-tri(OH)-12-[1,1-di(Me) prop-2-enyl]-2,2-di(Me)-2H-pyrano(3,2-*b*)xanthen-6-one	181	Mahabusarakam, 1992

Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. staudtii			
(stem bark)	rheediaxanthone A	18	Waterman and Hussain, 1982
G. subelliptica			
(pericarp)	12b-hydroxy-des-D-garcigerin A	38	Iinuma, *et al.*, 1996
	subelliptenone F	40	
(root bark)	subelliptenone A	190	Iinuma, *et al.*, 1994
	subelliptenone B	191	
	12b-hydroxy-des-D-garcigerin A	38	Iinuma, *et al.*, 1995c
	globuxanthone	57	
	subelliptenone C, D	59,60	
	subelliptenone E	192	Iinuma, *et al.*, 1995a
	subelliptenone F	40	
	subelliptenone G	42	
	1,5-di(OH)-3-(OMe)xanthone	131	
	subelliptenone H	194	Iinuma, *et al.*, 1995b
	subelliptenone I	193	
(stem bark)	globuxanthone	57	Waterman and Hussain, 1982
	rheediaxanthone-A	18	
(wood)	12b-hydroxy-des-D-garcigerin A	38	Fukuyama, *et al.*, 1991
	garciniaxanthone A	39	
	garciniaxanthone B	55	
	globuxanthone	57	

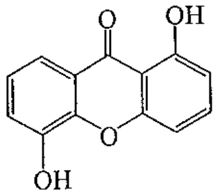
Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. subelliptica (wood)	garciniaxanthone C	202	Minami, *et al.*, 1994
	1,8-di(OH)-6-(OMe)xanthone	201	
	1,2,5-tri(OH)xanthone	196	
	2,6-di(OH)-1,5-di(OMe) xanthone	197	
	1,2-di(OH)-5,6-di(OMe) xanthone	198	
	1,6-di(OH)-5-(OMe)xanthone	16	
	1,5-di(OH)xanthone	1	
	garciniaxanthone D	56	Minami, *et al.*, 1995
	garciniaxanthone E	200	Minami, *et al.*, 1996a
	2,5-di(OH)-1-(OMe)xanthone	50	
	subelliptenone A	190	
	subelliptenone G	42	Minami , *et al.*, 1996b
	symphoxanthone	31	
	1-*O*-methylsymphoxanthone	32	
	garciniaxanthone F	203	
	garciniaxanthone H	204	
	garciniaxanthone G	53	
	1,6-di-*O*-methylsymphoxanthone	195	Minami , *et al.*, 1998

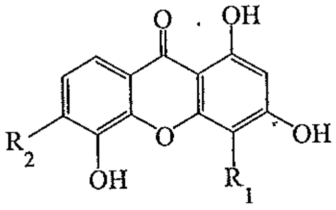
Table 1 (Continued)

Scientific name (Investigated part)	Xanthone compound	Structure	Bibliography
G. terpnophylla (wood)	mangostin euxanthone 1,5-di(OH)xanthone	141 33 1	Bandaranayake, *et al.*, 1975
G. thwaitesii (bark and timber)	2,5-di(OH)-1,6-di(OMe) xanthone	199	Gunatilaka, *et al.*, 1983
G. vilersiana (bark)	subelliptenone B subelliptenone H globuxanthone 1-*O*-methylglobuxanthone 12b-(OH)-des-D-garcigerrin-A symphoxanthone	191 194 57 58 38 31	Nguyen and Harrison, 2000
G.vitiensis (heart wood)	5,9-di(OH)-8-(OMe)-2,2-di(Me)-7-(3-methylbut-2-enyl)-2H,6H-pyrano[3,2-*b*]-xanthen-6-one	147	Ali, *et al.*, 1999
G. xanthochymus (fruit)	1,5-di(OH)xanthone 1,7-di(OH)xanthone (euxanthone)	1 33	Baslas and Kumar, 1979, 1981

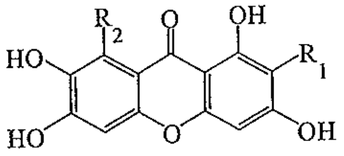
The structure of xanthones from *Garcinia* genus



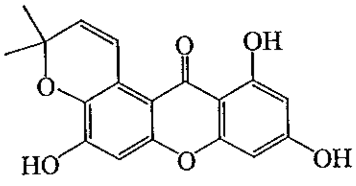
1 1,5-di(OH)xanthone



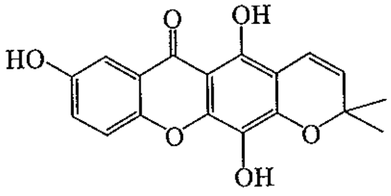
	R_1	R_2	
2	1,1-dimethylallyl	OH	: assiguxanthone A
6	H	H	: 1,3,5-tri(OH)xanthone
7	1,1-dimethylallyl	H	: pancixanthone A



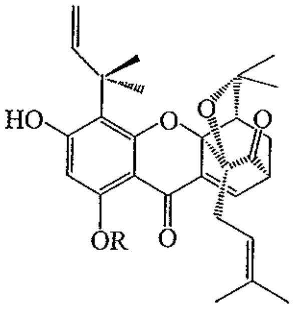
	R_1	R_2	
3	isoprenyl	H	: assiguxanthone B
4	H	isoprenyl	: 1,3,6,7-tetra(OH)-8-(3-(Me)but-2-enyl)xanthone



5 toxyloxanthone B

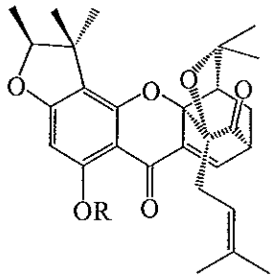


8 atroviridin



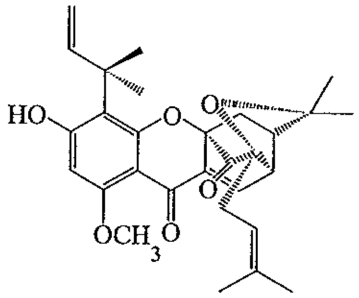
9 R=H : bractatin

10 R=Me : 1-*O*-methylbractatin

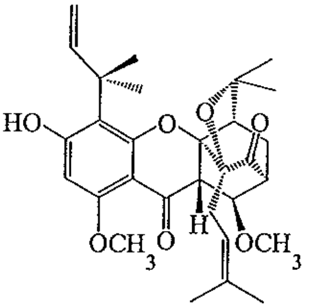


11 R=H : isobractatin

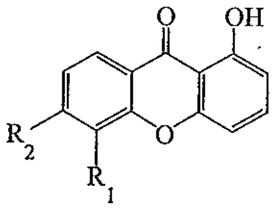
12 R=Me : 1-*O*-methylisobractatin



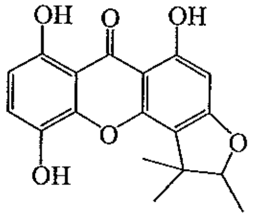
13 1-*O*-methylneobractatin



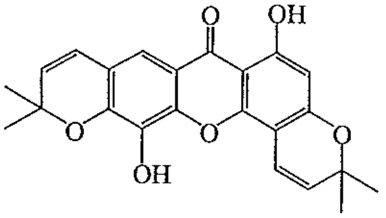
14 1-*O*-(Me)-8-(OMe)-8,8a-dihydrobractatin



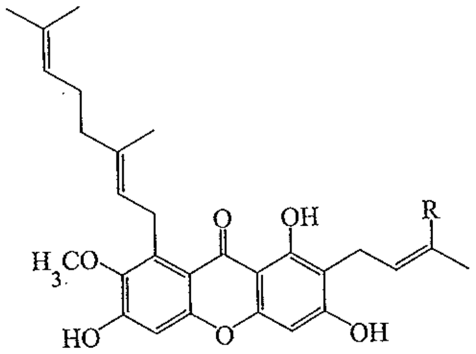
	R_1	R_2	
15	OH	OH	: 1,5,6-tri(OH)xanthone
16	OCH_3	OH	: buchanaxanthone



17 garbogiol



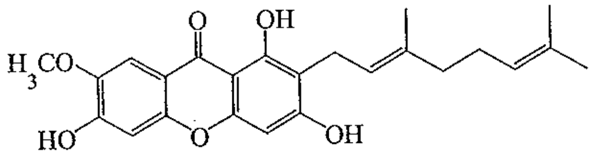
18 rheediaxanthone A



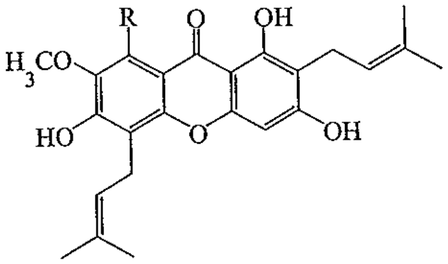
19 R = CH_3 : cowanin

20 R = CH_2OH : cowanol

21 R = H : rubraxanthone

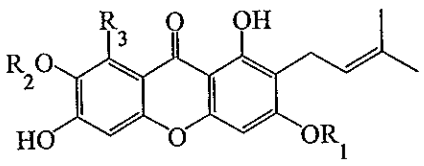


22 cowaxanthone

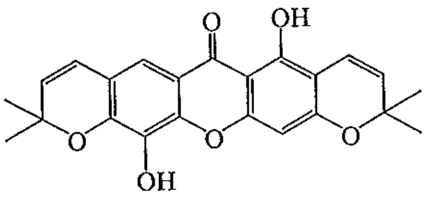


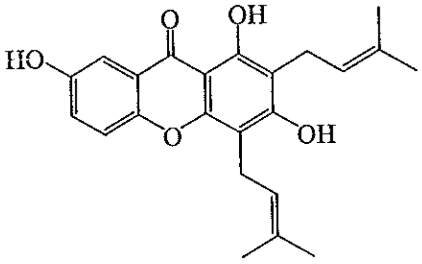
23 R = H : 1,3,6-tri(OH)-7-(OMe)-2,5-bis
(3-(Me)-2-butenyl)xanthone

24 R = prenyl : 7-*O*-methylgarcinone E



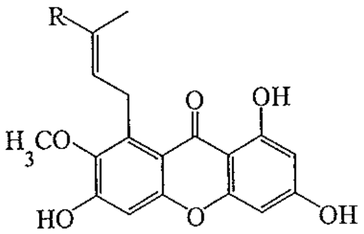
	R_1	R_2	R_3	
25	H	H	geranyl	: norcowanin
26	CH_3	CH_3	isoprenyl	: β-mangostin

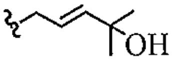


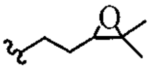


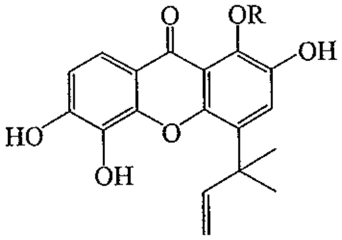
27 pyranojacareubin

28 1,3,7-tri(OH)-2,4-diisoprenylxanthone



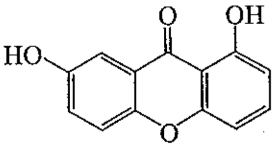
29 R =  : 1,3,6-tri(OH)-8-(7-(OH)-3,7-di(Me)-2,5-octadienyl)-7-(OMe)xanthone

30 R =  : 1,3,6-tri(OH)-8-(6,7-epoxy-3,7-di-(Me) -2-octenyl)-7-(OMe)xanthone

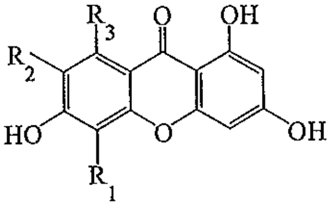


31 R = H : symphoxanthone

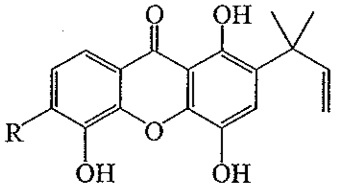
32 R = CH_3 : 1-*O*-(Me)symphoxanthone



33 1,7-di(OH)xanthone (euxanthone)



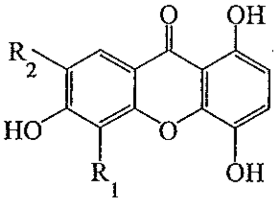
	R_1	R_2	R_3	
34	OH	geranyl	prenyl	: garciniaxanthone
35	H	OCH_3	H	: 1,3,6-tri(OH)-7-(OMe)xanthone
36	H	OCH_3	prenyl	: 1,3,6-tri(OH)-8-isoprenyl-7-(OMe)xanthone
37	OCH_3	H	H	: 1,3,6-tri(OH)-5-(OMe)xanthone



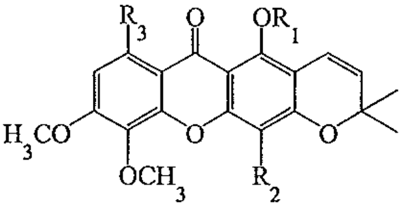
38 R = H : 12b-(OH) -des-D-garcigerin A

39 R = prenyl : garciniaxanthone A

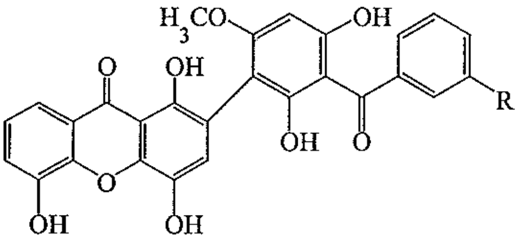
40 R = OH : subelliptenone F



	R_1	R_2	
41	OCH_3	prenyl	: 1,4,6-tri(OH)-5-(OMe)-7-(3-(Me)but-2-enyl)xanthone
42	H	H	: 1,4,5-tri(OH)xanthone

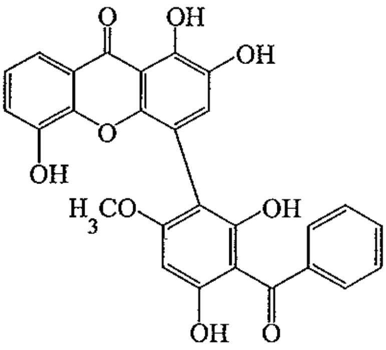


	R_1	R_2	R_3	
43	CH_3	OCH_3	H	: dulxanthone E
44	H	H	OCH_3	: dulxanthone F
45	H	OCH_3	OCH_3	: dulxanthone G
46	CH_3	OCH_3	OH	: dulxanthone H

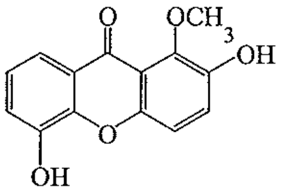


47 R = H : garciduol A

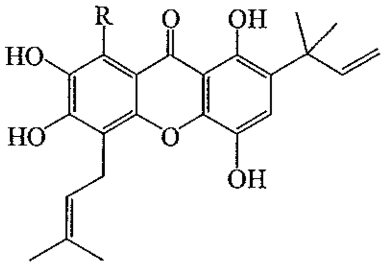
48 R = OH : garciduol B



49 garciduol C

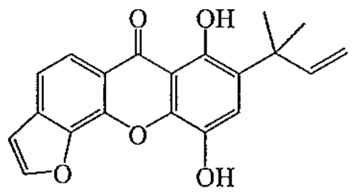


50 2,5-di(OH)-1-(OMe)xanthone

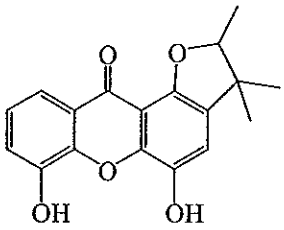


51 R = $CH_2CH=CMe_2$: dulciol B

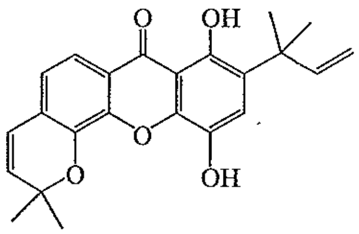
52 R = $CH_2CH_2C(OH)Me_2$: dulciol C



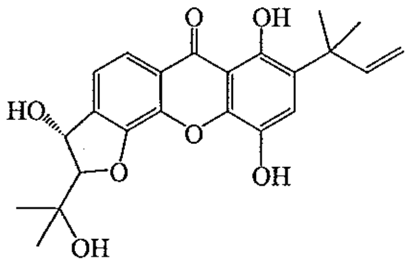
53 dulciol D



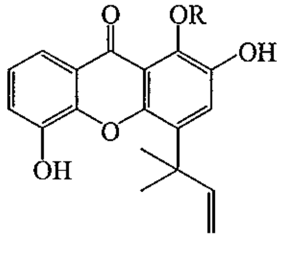
54 dulciol E



55 garciniaxanthone B

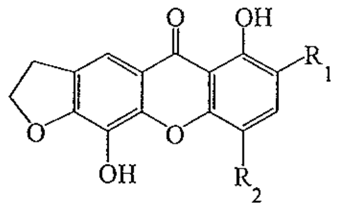


56 garciniaxanthone D

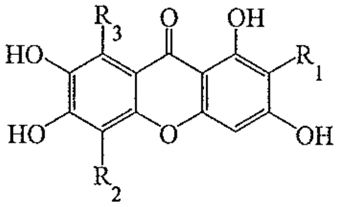


57 R = H : globuxanthone

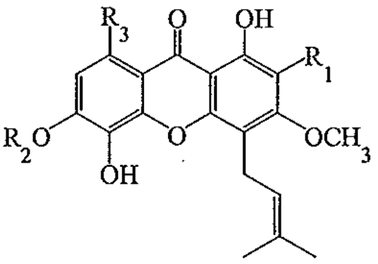
58 R = Me : 1-*O*-methylglobuxanthone



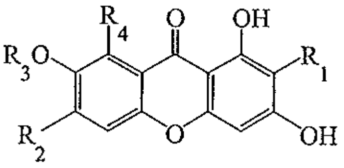
	R_1	R_2	
59	1,1-di(Me)allyl	OH	: subelliptenone C
60	OH	1,1di(Me)allyl	: subelliptenone D



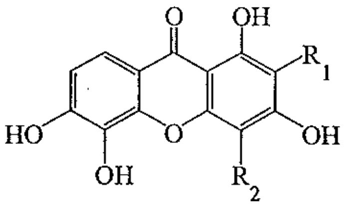
	R_1	R_2	R_3	
61	H	geranyl	prenyl	: dulciol A
62	H	H	H	: 1,3,6,7-tetra(OH)xanthone
63	glu	H	H	: glycoside of 1,3,6,7-tetra(OH)xanthone



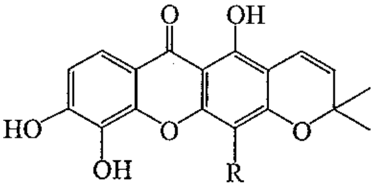
	R_1	R_2	R_3	
64	H	H	H	: dulxanthone A
65	prenyl	H	H	: dulxanthone B
66	H	CH_3	prenyl	: dulxanthone C



	R_1	R_2	R_3	R_4		
67	H	OH	CH_3	prenyl	:	dulxanthone D
68	H	H	H	H	:	gentisein
69	prenyl	H	H	H	:	1,3,7-tri(OH)2-(3-(Me)but-2-enyl)xanthone

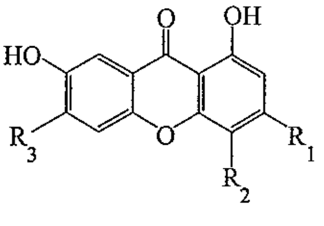


	R_1	R_2		
70	H	prenyl	:	ugaxanthone
71	prenyl	H	:	isoprenylxanthone

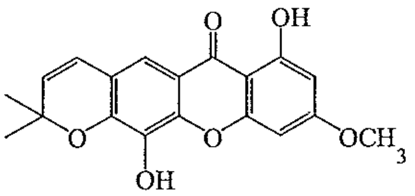


72 R = H : jacareubin

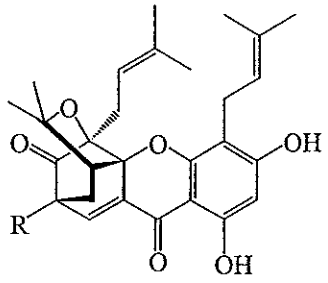
73 R = prenyl : xanthone VI



	R_1	R_2	R_3		
74	OCH_3	H	H	:	gentisin
75	OCH_3	OH	H	:	1,4,7-tri(OH)-3-(OMe)xanthone
76	H	H	OH	:	1,6,7-tri(OH)xanthone

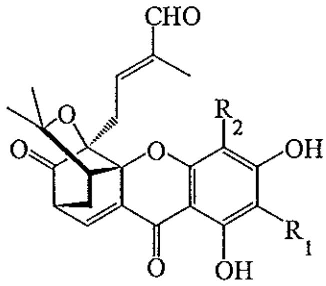


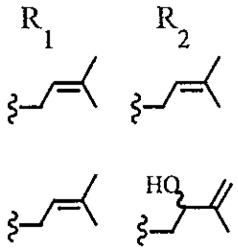
77 forbexanthone



78 R = H : forbesione

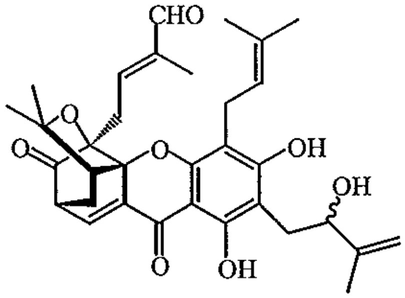
85 R = OCH_3 : gaudichaudione H





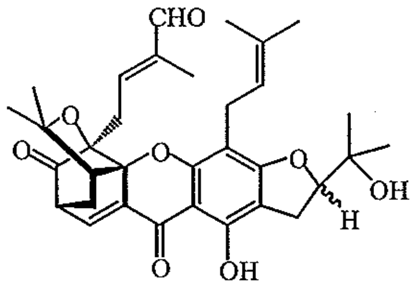
79 : gaudichaudione A

81 : gaudichaudione C



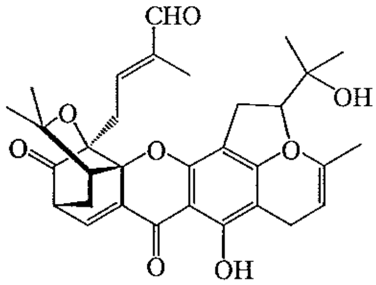
80 gaudichaudione B

84 diastereomer : gaudichaudione F

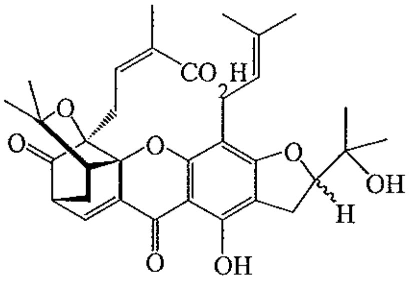


82 gaudichaudione D

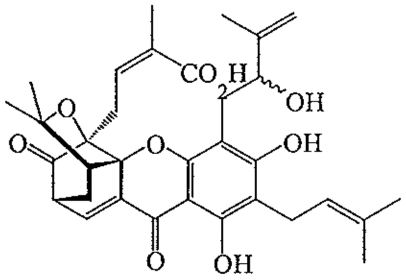
83 diastereomer : gaudichaudione E



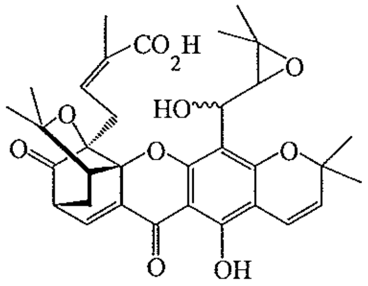
86 gaudichaudione G



87 gaudichaudiic acid A

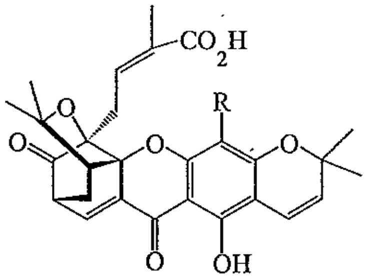


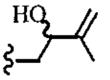
88 gaudichaudiic acid B

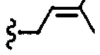


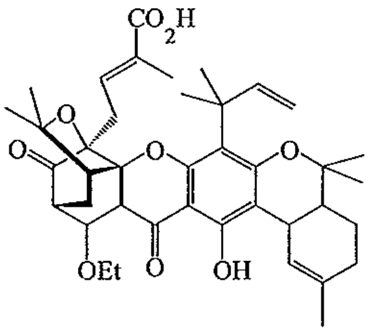
89 gaudichaudiic acid C

90 diastereomer: gaudichaudiic acid D

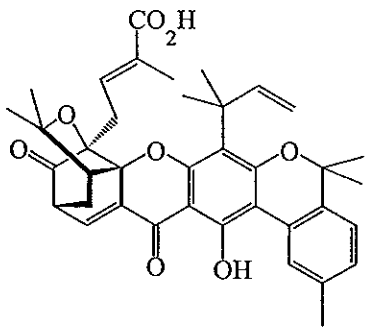


91 R =  : gaudichaudiic acid E

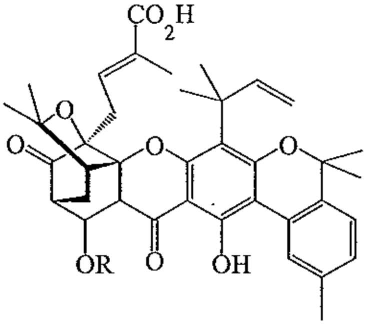
92 R =  : morellic acid



93 gaudichaudicc acid F

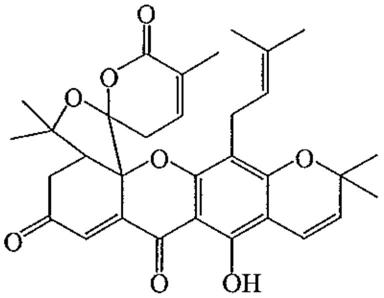


94 gaudichaudicc acid G

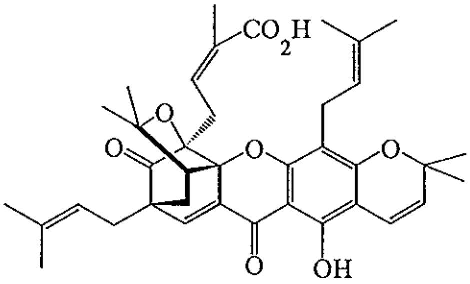


95 R = CH_3 : gaudichaudiic acid H

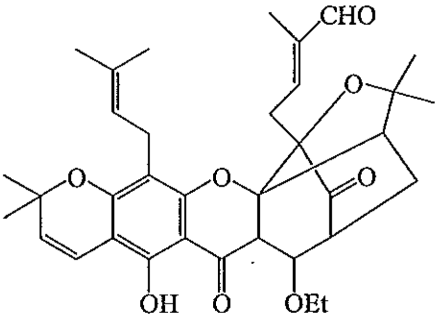
96 R = CH_2CH_3 : gaudichaudiic acid I



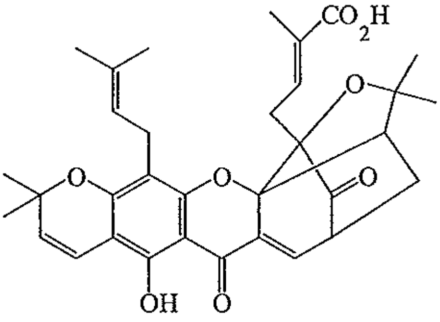
97 gaudispirolactone



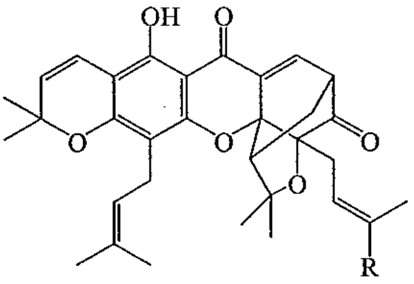
98 7-isoprenylmorellic acid



99 isomoreollin

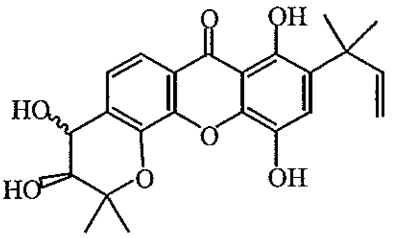


100 isomorellinol



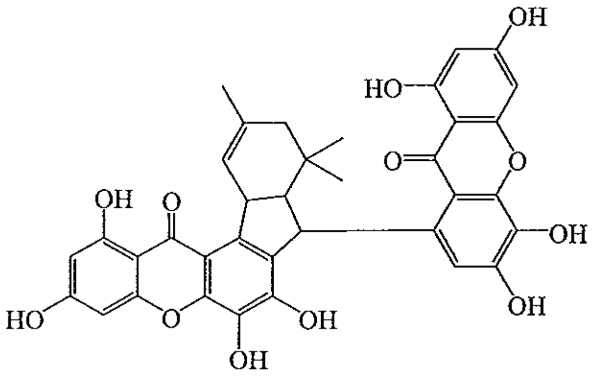
101 R = CHO : isomorellin

102 R = CO_2H : isomorellic acid

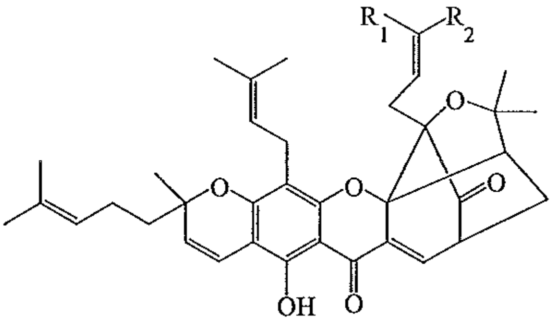


103 (cis) garcigerrin A

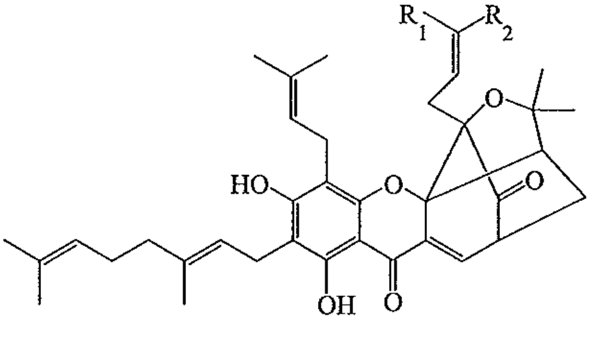
104 (trans) garcigerrin B



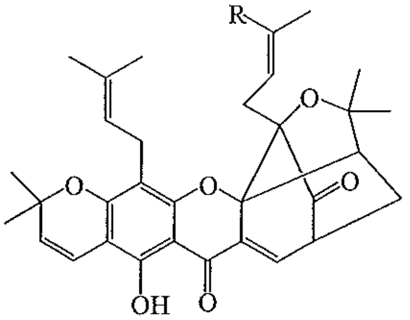
105 griffipavixanthone



	R_1	R_2	
106	CO_2H	CH_3	: gambogic acid
107	CH_3	CO_2H	: isogambogic acid
108	CH_3	CH_3	: gambogin

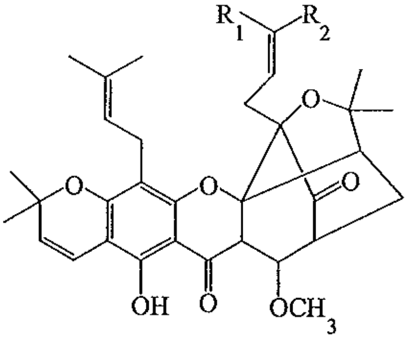


	R_1	R_2	
109	CHO	CH_3	: gambogenin
110	CH_3	CHO	: isogambogenin
111	CO_2H	CH_3	: gambogenic acid
112	CH_3	CH_3	: desoxygambogenin
113	$CH(OMe)_2$	CH_3	: gambogenin dimethyl acetal

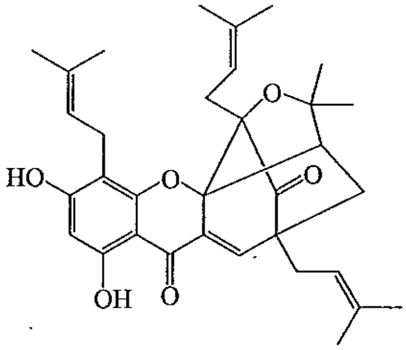


114 R = CH_3 : desoxymorellin

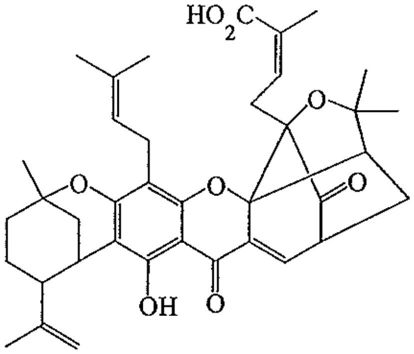
115 R = $CH(OMe)_2$: morellin dimethylacetal



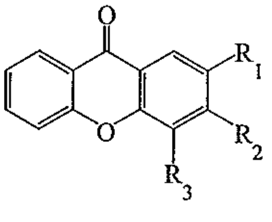
	R_1	R_2	
116	CH_3	CHO	: isomoreollin B
117	CO_2H	CH_3	: moreollic acid



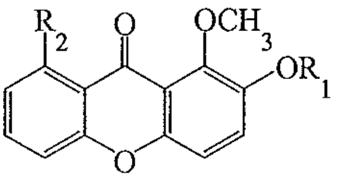
118 hanburin



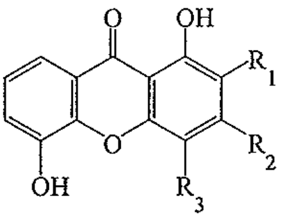
119 gambogellic acid



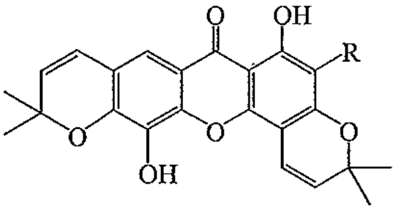
	R_1	R_2	R_3	
120	OH	H	H	: 2-(OH)xanthone
121	H	H	OH	: 4-(OH)xanthone
122	H	OH	OCH_3	: 3-(OH)-4-(OMe)xanthone



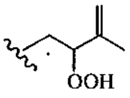
	R_1	R_2		
123	H	H	:	2-(OH)-1-(OMe)xanthone
124	H	CH_3	:	2-(OH)-1,8-di(OMe)xanthone
125	CH_3	H	:	1,2-di(OMe)xanthone
126	CH_3	CH_3	:	1,2,8-tri(OMe)xanthone

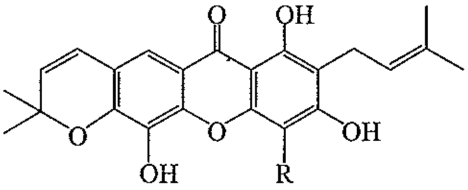


	R_1	R_2	R_3	
127	OCH_3	OH	H	: 1,3,5-tri(OH)-2-(OMe)xanthone
128	H	prenyl	OH	: 1,4,5-tri(OH)-3-(3-(Me)but-2-enyl)-9H-xanthen-9-one
129	H	OH	geranyl	: 1,3,5-tri(OH)-4-(3',7'-di(Me)octa-2',6'-dienyl)-9H-xanthen-9-one
130	geranyl	OH	H	: mangostinone
131	H	OCH_3	H	:1,5-di(OH)-3-(OMe)xanthone



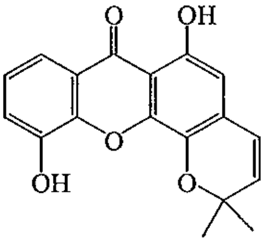
132 R = prenyl : latisxanthone A

133 R=  : latisxanthone B

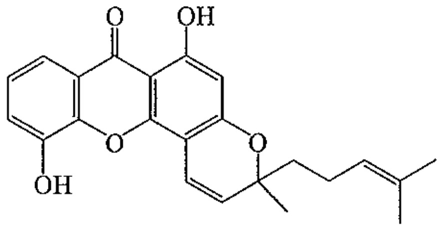


134 R = prenyl : latisxanthone C

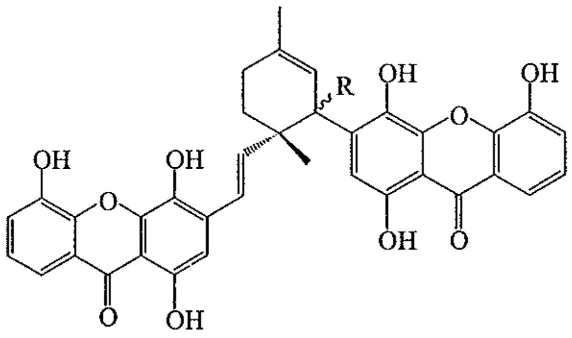
135 R = H : latisxanthone D



136 6,11-di(OH)-2,2-di(Me)-pyrano
[3,2-c]xanthen-7(2H)-one

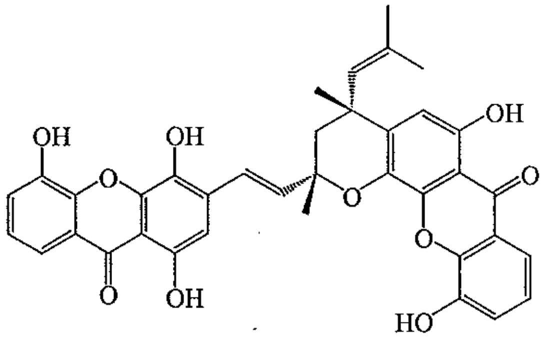


137 6,11-di(OH)-3-(Me)-3-(4-(Me)pent-3-enyl)-3H,7H-pyrano[2,3-c]xanthen-7-one

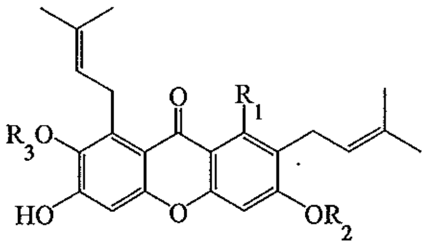


138 R = ◢H : garcilivin A

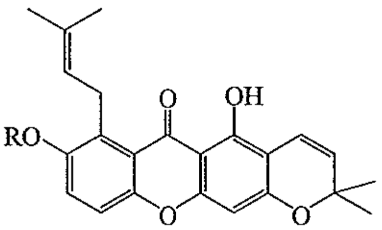
140 R = ⋯H : garcilivin C



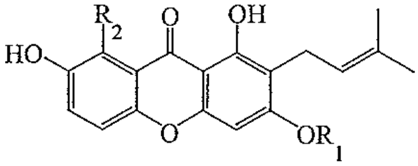
139 garcilivin B



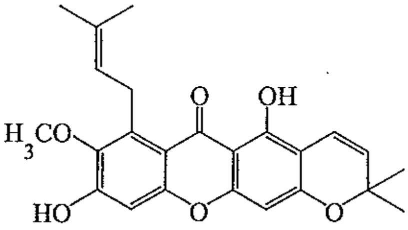
	R_1	R_2	R_3	
141	OH	H	CH_3	: mangostin
142	H	H	H	: normangostin



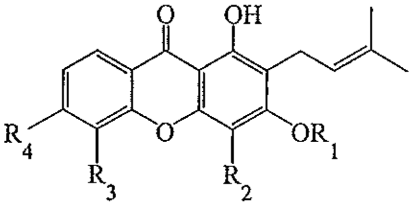
	R	
143	CH_3	: calabaxanthone
144	H	: demethylcalabaxanthone



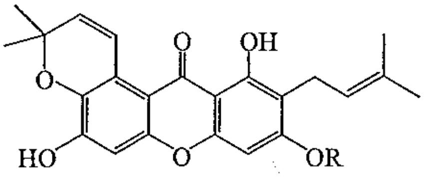
	R_1	R_2	
145	H	prenyl	: 1,3,7-tri(OH)-2,8-bis-(γ,γ-di(Me)allyl) xanthone
146	CH_3	H	: 1,7-di(OH)-3-(OMe)-2-(γ,γ-di(Me)allyl)-xanthone



147 5,9-di(OH)-8-(OMe)-2,2-di(Me)-7-(3-(Me)but-2-enyl)-2H,6H-pyrano[3,2-b]xanthen-6-one

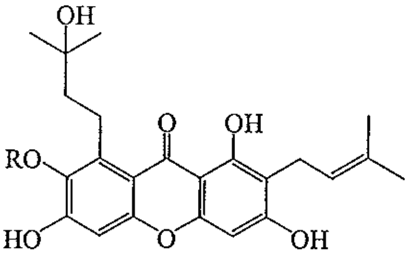


	R_1	R_2	R_3	R_4	
148	CH_3	H	OH	H	: 1,5-di(OH)-3-(OMe)-2-(3-(Me)but-2-enyl)xanthone
149	H	prenyl	H	OH	: garcinone A



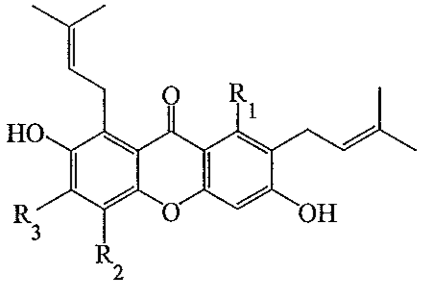
150 R = H : garcinone B

153 R = Me : 3-*O*-methylgarcinone B

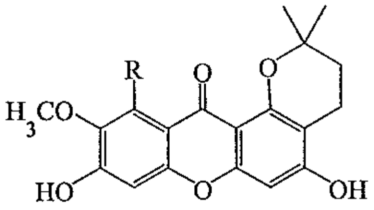


151 R = H : garcinone C

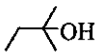
152 R = CH_3 : garcinone D

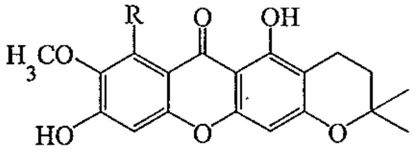


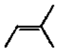
	R_1	R_2	R_3	
154	H	H	H	: 6-desoxy-γ-mangostin
155	OH	isoprenyl	OH	: garcinone E
156	OH	isoprenyl	OMe	: 1,3,7-tri(OH)-2,5,8-tris-(3-(Me) but-2-enyl-6-(OMe)xanthone

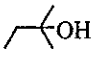


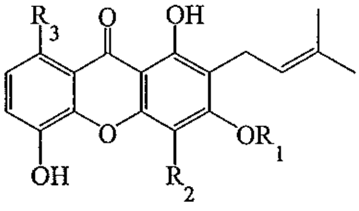
157 R =  : 1-isomangostin

158 R =  : 1-isomangostin hydrate

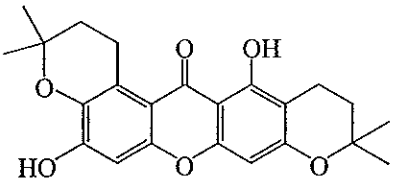


159 R =  : 3-isomangostin

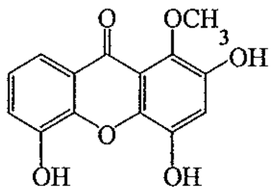
160 R =  : 3-isomangostin hydrate



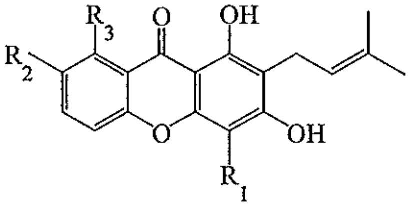
	R_1	R_2	R_3	
161	H	prenyl	OH	: gartanin
162	H	prenyl	H	: 8-desoxygartanin
163	CH_3	H	OH	: 1,5,8-tri(OH)-3-(OMe)-2-(3-(Me)but-2-enyl)xanthone



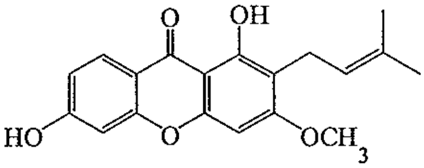
164 BR-xanthone-A



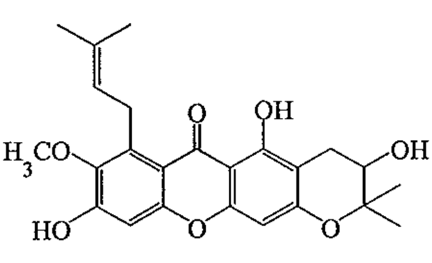
165 BR-xanthone-B



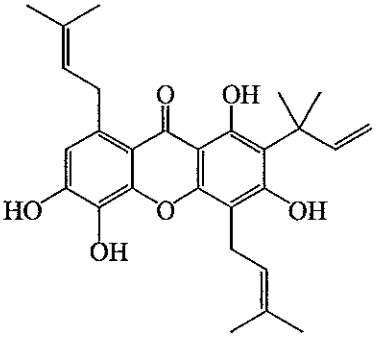
	R_1	R_2	R_3	
166	Me	prenyl	OH	: 2,7-di-(3-methylbut-2-enyl)-1,3,8-tri(OH)-4-(Me)xanthone
167	H	CO_2H	prenyl	: 2,8-di-(3-methylbut-2-enyl)-7-carboxy-1,3-di(OH)xanthone



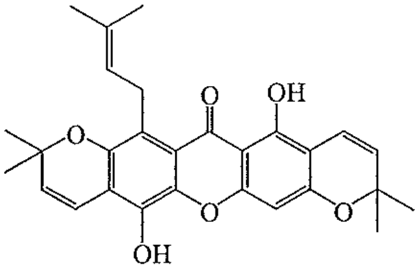
168 1,6-di(OH)-3-(OMe)-2-(3-(Me)-2-butenyl)xanthone



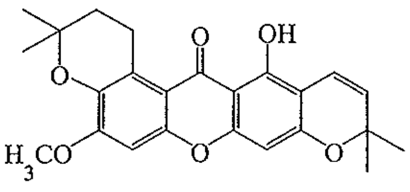
169 mangostanol



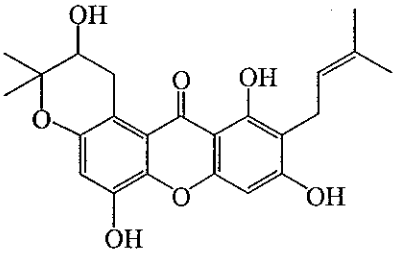
170 nervosaxanthone



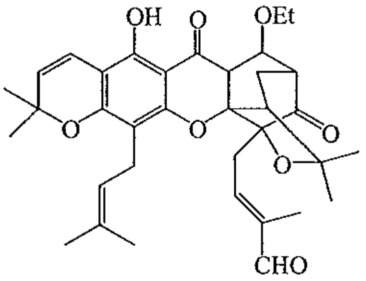
171 garcimangosone A



172 garcimangosone B

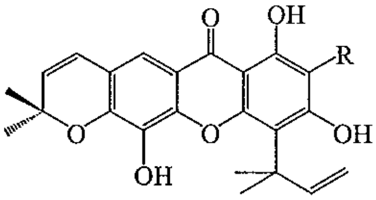


173 garcimangosone C



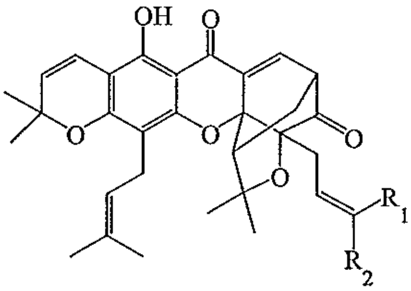
174 moreollin

(ethoxydihydroisomorelin)

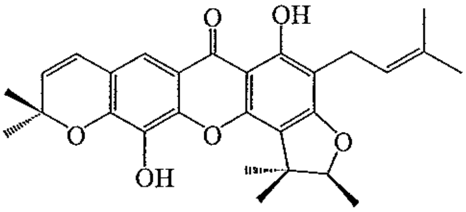


175 R = H : 1,3,5-tri(OH)-6',6'-di(Me)pyrano(2',3':6,7)-4-(1,1-di(Me)prop-2-enyl)xanthone

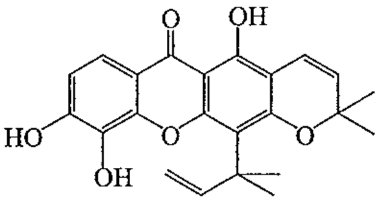
176 R = prenyl : 1,3,5-tri(OH)-6',6'-di(Me)pyrano(2',3':6,7)-2-(3-(Me)but-2-enyl)-4-(1,1-di(Me)prop-2-enyl)xanthone



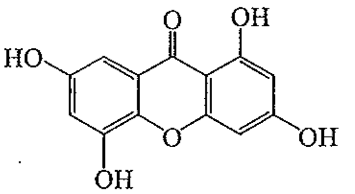
	R_1	R_2	
177	Me	CO_2H	: isomoreollic acid
178	CHO	Me	: morellin
179	Me	CHO(dihydro)	: dihydroisomorellin



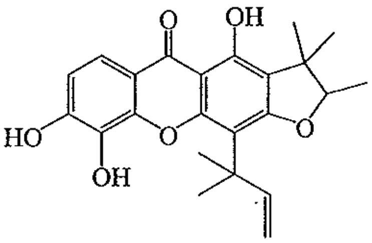
180 4",5"-dihydro-1,5-di(OH)-6',6'-di(Me)pyrano(2',3':6,7)-2-(3-(Me)but-2-enyl)-4",4",5"-tri(Me)furano(2",3":3,4)xanthone



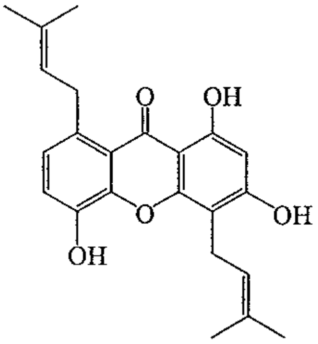
181 macluraxanthone



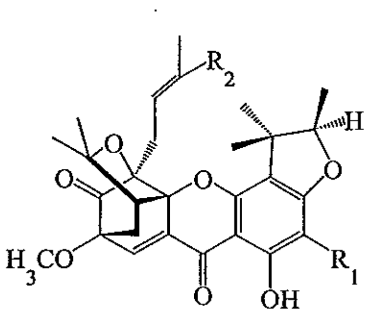
182 1,3,5,7-tetra(OH)xanthone

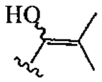


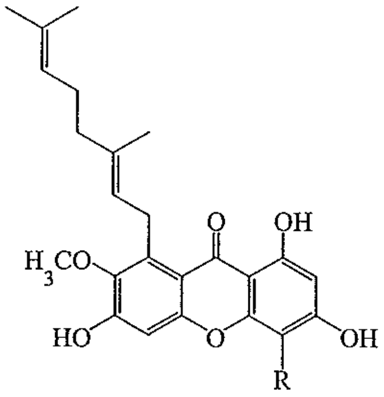
183 isorheediaxanthone B



184 1,3,5-tri(OH)-4,8-bis(3',3'-di(Me)allyl)xanthone

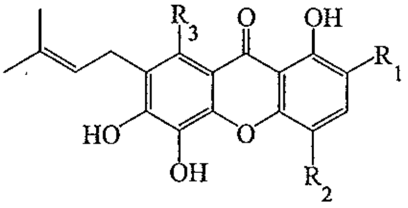


	R_1	R_2	
185	CH_3	prenyl	: scortechinone A
186	CO_2H	prenyl	: scortechinone B
187	CO_2H		: scortechinone C

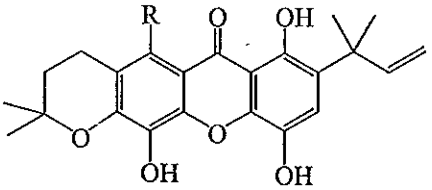


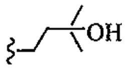
188 R = $CH_2CH{=}C(Me_2)$: isocowanin

189 R = $CH_2CH{=}C(Me)CH_2OH$: isocowanol

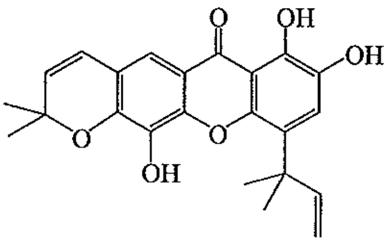


	R_1	R_2	R_3	
190	1,1-di(Me)allyl	OH	prenyl	: subelliptenone A
191	OH	1,1-di(Me)allyl	H	: subelliptenone B

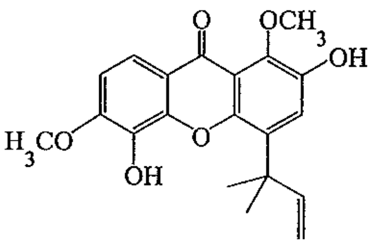


192 R =  : subelliptenone E

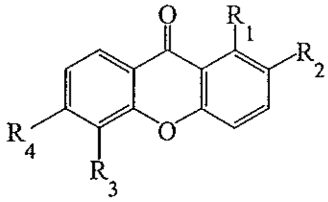
193 R = H : subelliptenone I



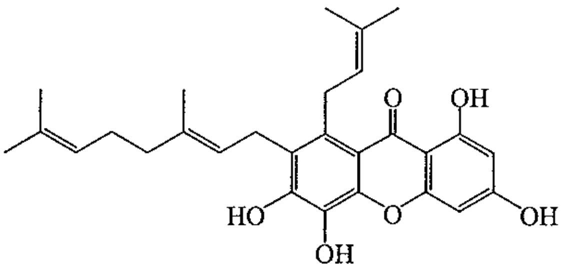
194 subelliptenone H



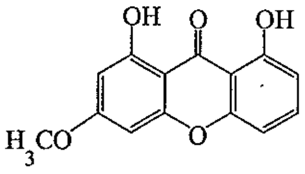
195 1,6-di(OMe)symphoxanthone



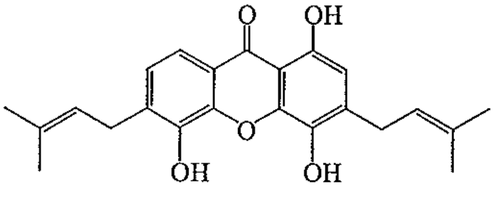
	R_1	R_2	R_3	R_4	
196	OH	OH	OH	H	: 1,2,5-tri(OH)xanthone
197	OMe	OH	OMe	OH	: 2,6-di(OH)-1,5-di(OMe)xanthone
198	OH	OH	OMe	OMe	: 1,2-di(OH)-5,6-di(OMe)xanthone
199	OMe	OH	OH	OMe	: 2,5-di(OH)-1,6-di(OMe)xanthone



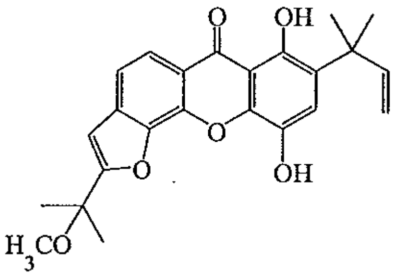
200 garciniaxanthone E



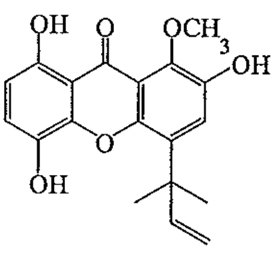
201 1,8-di(OH)-6-(OMe)xanthone



202 garciniaxanthone C



203 garciniaxanthone F



204 garciniaxanthone H

1.3 The Chemical Constituents from *Garcinia cowa*

The *Garcinia cowa* was first investigated by Krahn in 1968. Cowanin (**19**), cowanol (**20**) and cowaxanthone (**21**) were isolated from the stem. Further study by Lee and Chan in 1977, 1,3,6-tri(OH)-7-(OMe)-8-(3,7-dimethyl-2,6-octadienyl) xanthone (**23**) was isolated. In 1994 Na Pattalung isolated 1,3,6-tri(OH)-7-(OMe)-2,5-bis(3-methyl-2-butenyl)xanthone (**22**) and norcowanin (**25**) from the latex and in 1977, 7-*O*-methylgarcinone E (**24**) and *β*-mangostin (**26**) were reported to obtained from the stem bark by Likhitwitayawuid.

1.4 The Biological Activities of *Garcinia cowa*

Garcinia cowa Roxb. (Guttiferae) has been used in the folk medicine for variety purposes. The bark has been used in traditional medicine as an antipyretic, antimicrobial agent (Na Pattalung, *et al.*, 1994), in addition it was used as pesticide and mosquito larvicide (Maikhuri and Gangwar, 1993). The sun dried fruit was used to treat dysentery (Rao, *et al.*, 1981). The methanolic extract of leaf (fresh and dried) has been reported to show strong antitumor-promoting activity (Maurakami, *et al.*, 1995 and 1997). In Malaysia, an ether extract from dried leaf has been reported in inflammation induction and exhibition of epstein-barr virus early antigen induction (Ilham, *et al.*, 1995). The latex from trunks and the roots are used as antifever agent (Na Pattalung, *et al.*, 1994). The pure compounds (cowanin, cowanol, cowaxanthone, 7-*O*-methylgarcinone E and *β*-mangostin) and ninety-five percentage aqueous ethanols of dried stem bark have been reported to have antimalarial activity (Likhitwitayawuid, *et al.*, 1998a).

Although a number of biological properties of xanthones from *Garcinia cowa* Roxb., such as antimalarial, antimicrobial activity have been recognized, no study on the antioxidant potential of this group of natural products has been described. Natural antioxidants have attracted attention because some synthetic antioxidants have been found to be carcinogenic and harmful to lungs and liver (Yamasaki, *et al.*, 1994). Since most xanthones that occur in all higher plants and in various parts of the plant have phenolic functional groups on a linear tricyclic ring, they are anticipated to have antioxidant activity. In addition, several xanthone compounds from *Garcinia* genus have been reported to show antioxidation activity such as xanthones 1,4,5-trihydroxy-3,6-bis (3-methyl-2-butenyl)xanthone, 1,2,5-trihydroxyxanthone, Garciniaxanthones F, G and H from the wood of *Garcinia subelliptica* (Minami, *et al.*, 1994 and 1996).

1. 5 The Objective

Analytical TLC of the latex of *G. cowa* indicated that apart from five previously reported xanthones, some more chemical constituents in the latex are of interest. The preliminary testing on radical scavenging of the crude material also exhibits potent activity. It then prompted us to investigate the components of *G. cowa* more thoroughly and search for the antioxidation activity of pure compounds.

CHAPTER 2

EXPERIMENTAL

2.1 General Method

Ultraviolet spectra were recorded on a UV-160A spectrophotometer (SHIMADZU). Principle absorption bands (λ_{max}) were recorded in wavelengths (nm) and log ε in ethanol solution. Infrared spectra were recorded on FTS165 FT-IR spectrophotometer in wavenumber (cm^{-1}). ^1H and ^{13}C-nuclear magnetic resonance spectra were recorded on Varian UNITY INOVA 500 MHz FT-NMR, operating at 500 MHz (^1H) and 125 MHz (^{13}C), using $CDCl_3$ solution (a few drops of DMSO-d_6 being added whenever necessary) with tetramethylsilanes (TMS) as internal standard. The spectra were recorded as chemical shifts parameter (δ) value in ppm down field from TMS. Inverse-detected heteronuclear correlations were measured using HMQC and HMBC pulse sequences with a pulse field gradient. Melting points were measured in centigrade (°C) and are uncorrected. It was measured on a digital Electrothermal 9100 Melting Point Apparatus. Optical rotation was measured in ethanol solution with sodium D line (590 nm) on an AUTOPOL®II automatic polarimeter. Quick column chromatography was performed on silica gel 60 H (Merck). Column chromatography utilized silica gel 100 (70-230 Mesh ASTM) (Merck). Pre-coated TLC aluminum sheets of silica gel 60 GF_{254} (20x20 cm, layer thickness 0.2 mm) (Merck) were used for analytical purposes and the compounds were visualized under UV light. Preparative thin-layer chromatography was carried out on glass plates using silica gel 60 GF_{254} (20x20 cm, layer thickness 2 mm)(Merck). Bands were detected by exposure to short wavelength ultraviolet light. All organic solvents for extraction and chromatography were distilled at their boiling point ranges prior to use. The analytical grade of ethanol and α,α-diphenyl-β-picrylhydrazyl (DPPH) free radical were used in the testing of antioxidation activity. The absorptions of the test solution were detected with a Spectronic 21 (MILTON ROY).

2.2 Plant Material

The latex of *Garcinia cowa* Roxb. (Guttiferae) was collected from Samtambon district, amphur Chulabhorn, Nakhon Sri Thammarat province in the Southern part of Thailand. A herbarium specimen has been deposited in the herbarium of the Department of Biology, Faculty of Science, Prince of Songkla University, Thailand.

2.3 Extraction and Isolation

The latex (38.16 g) which was contaminated with bark material was treated with warm acetone and the mixture was filtered to remove the bark material. A crude material was obtained as a yellow - brown viscous liquid (35.00 g) after removal of the solvent under reduced pressure. Its TLC, using 100% dichloromethane as a mobile phase, showed several purple spots under UV light. It was slightly soluble in hexane, moderately soluble in dichloromethane and very soluble in acetone and methanol. The crude material was chromatographed on quick column chromatography over silica gel. Elution was conducted with hexane, hexane-dichloromethane, dichloromethane, dichloromethane-acetone, acetone and finally with methanol. On the basis of their TLC characteristics, the collected fractions which contained the same major components were combined to afford nine fractions (A-I) as shown in Table 2. The selected fractions were further purified to afford **PGC 1-12** (Figure 1).

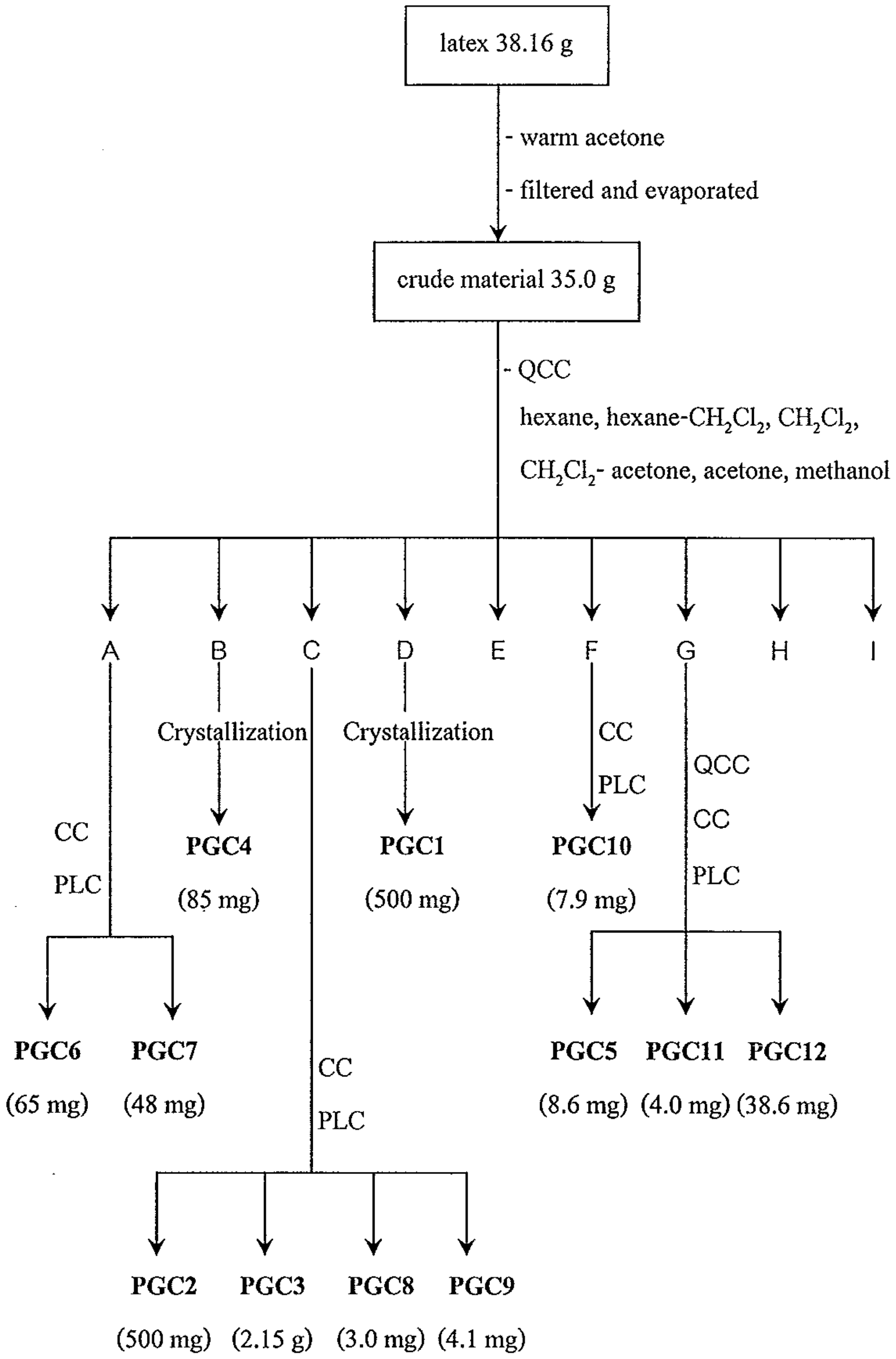


Figure 1 Isolation of compounds **PGC 1-12** from the latex of *G. cowa*

Table 2 Fractions obtained from crude material by quick column chromatography

Fraction	weight (g)	physical characteristic
A	5.312	yellow viscous-liquid
B	0.127	yellow solid mixed with yellow viscous liquid
C	5.562	yellow solid mixed with yellow viscous liquid
D	0.530	bright yellow needles
E	0.601	brown-yellow viscous-liquid
F	7.108	brown viscous-liquid
G	12.653	brown viscous-liquid
H	0.382	red-brown solid
I	1.126	brown viscous-liquid

2.4 Chemical Investigation

Purification of fraction A

Fraction A (5.312 g) was further fractionated by column chromatography and eluted with 60% hexane in dichloromethane. Fractions with the similar TLC chromatograms were combined and evaporated under reduced pressure to afford eight fractions (A1-A8).

Isolation of PGC6 and PGC7

Fraction A4 (1.9026 g) contained three major components. On the chromatogram, two components were visualized under UV light and the other one appeared as a brown spot after the chromatogram was left at room temperature over night. Rechromatographed of fraction A4 on column chromatography and eluted with hexane-dichloromethane gave the mixture of two major purple fluorescent spots (1.326 g). The mixture (1.326 g) was further purified by preparative TLC on silica gel plates, developing with 40% dichloromethane in hexane gave two isolated bands. A red-brown viscous liquid of PGC6 (0.0652 g) was obtained from the first band (R_f 0.45, 50% hexane in dichloromethane). The second band gave a red-brown viscous liquid PGC7 (0.0480 g) (R_f 0.41, 50% hexane in dichloromethane).

PGC6

UV (EtOH) λ_{max} nm (log ε)		331 (4.44), 290 (4.85), 238 (4.54)
FT-IR (neat) ν (cm^{-1})		3404 (O-H stretching) 1648 (C=O stretching)
^{1}H NMR ($CDCl_3$)(δ ppm)		13.74 (*s*, 1H), 6.83 (*s*, 1H), 6.73 (*dd*, *J* 10.0 and 0.5 Hz, 1H), 6.24 (*s*, 1H), 5.57 (*d*, *J* 10.0 Hz, 1H), 5.27 (*dt*, *J* 6.5, 1.5 Hz, 1H), 5.03 (*br t*, *J* 6.5 Hz, 1H), 4.09 (*br d*, *J* 6.0 Hz, 2H), 3.80 (*s*, 3H), 2.03-2.07 (*m*, 2H), 2.00-2.02 (*m*, 2H), 1.83 (*d*, *J* 0.5 Hz, 3H), 1.60 (*d*, *J* 0.5 Hz, 3H), 1.55 (*s*, 3H), 1.47 (*s*, 3Hx2)
^{13}C NMR ($CDCl_3$)(δ ppm)		181.93, 159.83, 157.91, 156.24, 155.70, 154.58, 142.69, 137.07, 135.61, 131.29, 127.12, 124.28, 123.20, 115.72, 112.18, 104.48, 103.70, 101.66, 94.15, 77.92, 62.02, 39.74, 28.30, 26.55, 26.48, 25.63, 17.67, 16.49
DEPT 135°	CH_3 :	28.30, 25.63, 17.67, 16.49
	CH_2 :	39.71, 26.55, 26.48
	CH :	127.12,124.28, 123.20, 115.72, 101.66, 94.15

PGC7

UV (EtOH) λ_{max} nm (log ε)	362 (4.09), 315 (4.62), 246 (4.85)
FT-IR (neat) ν (cm^{-1})	3418 (O-H stretching) 1641 (C=O stretching)
^{1}H NMR (CDCl$_3$)(δ ppm)	13.89 (*s*, 1H), 6.34 (*s*, 1H), 5.31 (*br t*, *J* 6.5 Hz, 1H), 5.29 (*br t*, *J* 6.5 Hz, 1H), 5.27 (*br t*, *J* 6.5 Hz, 1H), 5.03 (*br t*, *J* 7.0 Hz, 1H), 4.08 (*br d*, *J* 6.0 Hz, 2H), 3.80 (*s*, 3H), 3.57 (*br d*, *J* 7.5 Hz, 2H), 3.46 (*br d*, *J* 7.0 Hz, 2H), 2.03-2.08 (*m*, 2H), 1.90-2.02 (*m*, 2H), 1.88 (*d*, *J* 0.5 Hz, 3H), 1.85 (*d*, *J* 0.5 Hz, 3H), 1.83 (*d*, *J* 1.0 Hz, 3H), 1.78 (*d*, *J* 1.0 Hz, 3H), 1.69 (*d*, *J* 1.0 Hz, 3H), 1.60 (*d*, *J* 1.0 Hz, 3H), 1.55 (*d*, *J* 0.5 Hz, 3H)
^{13}C NMR (CDCl$_3$)(δ ppm)	182.38, 161.51, 160.56, 155.04, 153.52, 152.28, 142.28, 135.67, 135.29, 133.90, 132.67, 131.26, 124.32, 123.59, 121.54, 121.14, 113.93, 111.96, 108.36, 103.56, 93.23, 39.72, 26.57, 26.34, 25.86, 25.80, 22.64, 21.22, 17.97, 17.93, 17.67, 16.46
DEPT 135°	CH$_3$: 25.86, 25.80, 25.62, 17.97, 17.93, 17.67, 16.46
	CH$_2$: 39.72, 26.57, 26.34, 22.64, 21.22
	CH : 124.32, 123.59, 121.54, 121.14, 93.23

Isolation of PGC4

Fraction B (0.127 g) which contained one major component was recrystallized in the mixure of hexane-dichloromethane (4:1) to give **PGC4** (0.0852 g) as a bright yellow solid (R$_f$ 0.50 in 50% dichloromethane in hexane).

Melting point	222-224°
UV (EtOH) λ_{max} nm (log ε)	362 (3.66), 318 (4.01), 259 (4.21), 240 (4.19)
FT-IR (KBr) ν (cm^{-1})	3382 (O-H stretching) 1646 (C=O stretching)

^{1}H NMR (CDCl$_3$)(δ ppm)		13.48 (*s*, 1H), 7.51 (*s*, 1H), 6.43 (*s*, 1H), 6.21 (*s*, 1H), 5.31 (*br t*, *J* 7.5 Hz, 1H), 5.29 (*br t*, *J* 7.0 Hz, 1H), 4.00 (*s*, 3H), 3.62 (*br d*, *J* 7.5 Hz, 2H), 3.49 (*br d*, *J* 7.5 Hz, 2H), 1.88 (*s*, 3H), 1.86 (*s*, 3H), 1.79 (*s*, 3H), 1.69 (*s*, 3H)
^{13}C NMR (CDCl$_3$)(δ ppm)		180.31, 161.84, 160.15, 156.02, 150.47, 149.93, 143.98, 136.01, 132.76, 121.33, 120.90, 115.47, 113.01, 108.44, 101.99, 94.07, 56.40, 25.82, 25.74, 22.39, 21.44, 17.93
DEPT 135°	CH_3 :	25.82, 25.74, 17.93x2
	CH_2 :	22.39, 21.44
	CH :	121.33, 120.90, 101.99, 94.07

Isolation of PGC2, PGC3, PGC8 and PGC9

Fraction C (5.562 g) was crystallized in hexane-dichloromethane upon standing at room temperature to give a yellow solid (2.260 g) and the filtrate (3.20 g). The yellow solid was further purified by column chromatography using dichloromethane as an eluent to afford pure **PGC3** as pale yellow needles (2.151 g).

Melting point	123-123.5°
UV (EtOH) λ_{max} nm(log ε)	355 (3.90), 316 (4.41), 255 (4.47), 244 (4.57), 212 (4.55)
FT-IR (KBr) ν (cm^{-1})	3365 (O-H stretching) 1646 (C=O stretching)
^{1}H NMR (CDCl$_3$)(δ ppm)	13.83 (*s*, 1H), 6.85 (*s*, 1H), 6.32 (*s*, 1H), 5.48 (*dt*, *J* 7.0, 1.5 Hz, 1H), 5.28 (*dt*, *J* 7.0, 1.5 Hz, 1H), 5.04 (*br t*, *J* 7.0 Hz, 1H), 4.37 (*s*, 2H), 4.12 (*br d*, *J* 7.0 Hz, 2H), 3.82 (*s*, 3H), 3.54 (*br d*, *J* 7.0 Hz, 2H), 2.04-2.08 (*m*, 2H), 2.00-2.03 (*m*, 2H), 1.84 (*s*, 3H), 1.79 (*s*, 3H), 1.61 (*s*, 3H), 1.56 (*s*, 3H)

The filtrate of fraction C (3.20 g) was further purified by column chromatography and eluted with hexane-dichloromethane in polarity gradient manner. The eluents containing similar components were combined into seven fractions (C1-C7).

Fraction C3 (0.0531 g) was rechromatographed on column chromatography, eluting with hexane-dichloromethane and dichloromethane. The first fraction was further purified by preparative TLC, eluting with dichloromethane gave two isolated bands. Pale yellow solid of **PGC8** (0.0032 g) and **PGC9** (0.0041g) were obtained from the first and second band, respectively.

PGC8

Melting point		252-253°
UV (EtOH) λ_{max} nm (log ε)		360 (3.77), 319 (4.15), 300 (3.99), 260 (4.34), 242 (4.30)
FT-IR (KBr) ν (cm^{-1})		3216 (O-H stretching) 1655 (C=O stretching)
^{1}H NMR (CDCl$_3$)(δ ppm)		13.00 (*s*, 1H), 7.61 (*s*, 1H), 6.94 (*s*, 1H), 6.43 (*s*, 1H), 6.34 (*s*, 1H), 5.24 (*br t*, *J* 7.0 Hz, 1H), 4.01 (*s*, 3H), 3.92 (s, 3H), 3.37 (*br d*, *J* 6.5 Hz, 2H), 1.80 (*s*, 3H), 1.68 (*d*, *J* 1.0 Hz, 3H)
^{13}C NMR (CDCl$_3$)(δ ppm)		179.86, 163.85, 159.36, 156.24, 152.54, 152.37, 144.32, 131.83, 122.21, 113.63, 111.76, 104.62, 102.49, 89.58, 56.53, 55.90, 25.80, 21.36, 17.80
DEPT 135°	CH$_3$:	25.80, 17.80
	CH$_2$:	21.36
	CH :	122.21, 104.62, 102.49, 89.58

PGC9

Melting point	152-153°
UV (EtOH) λ_{max} nm (log ε)	345 (3.92), 315 (4.47), 281 (4.20), 246 (4.72)
FT-IR (KBr) ν (cm^{-1})	3375 (O-H stretching) 1652 (C=O stretching)
^{1}H NMR ($CDCl_3$)(δ ppm)	13.00 (*s*, 1H), 7.95 (*d*, *J* 9.0 Hz, 1H), 6.98 (*d*, *J* 9.0 Hz, 1H), 6.48 (*s*, 1H), 6.29 (*s*, 1H), 5.23 (*br t*, *J* 7.0 Hz, 1H), 4.02 (*s*, 3H), 3.95 (*s*, 3H), 3.38 (*br d*, *J* 7.0 Hz, 2H), 1.80 (*s*, 3H), 1.68 (*d*, *J* 1.5 Hz, 3H)
^{13}C NMR ($CDCl_3$)(δ ppm)	180.07, 164.08, 159.78, 155.70, 154.11, 149.53, 133.59, 131.93, 122.03, 122.00, 115.26, 112.34, 112.24, 103.24, 89.78, 61.95, 55.97, 25.78, 21.59, 17.78
DEPT 135°	CH_3 : 25.78, 17.78
	CH_2 : 21.59
	CH : 122.03, 122.00, 112.24, 89.78

Fraction C4 (1.6425 g) was a yellow solid which contained three components. The solid was chromatographed on column chromatography over silica gel. Elution was conducted with hexane-dichloromethane solvent system. The fractions containing similar components were combined into three fractions. Crystallization of the second fraction gave pure yellow solid of **PGC2** (0.500g) (R_f 0.55, in 3% methanol-dichloromethane).

Melting point	136-137°
UV (EtOH) λ_{max} nm(log ε)	355 (3.90), 316 (4.39), 255 (4.46), 242 (4.55), 212 (4.50)
FT-IR (KBr) ν (cm^{-1})	3425 (O-H stretching) 1636 (C=O stretching)

^{1}H NMR (CDCl$_3$)(δ ppm)	13.70 (*s*, 1H), 6.83 (*s*, 1H), 6.30 (*s*, 1H), 5.29 (*br t*, *J* 7.0 Hz, 1H), 5.26 (*br t*, *J* 7.0 Hz, 1H), 5.03 (*br t*, *J* 6.5 Hz, 1H), 4.10 (*br d*, *J* 7.0 Hz, 2H), 3.80 (*s*, 3H), 3.45 (*br d*, *J* 7.0 Hz, 2H), 2.02-2.07 (*m*, 2H), 1.97-2.00 (*m*, 2H), 1.84 (*s*, 3H), 1.80 (*s*, 3H), 1.78 (*s*, 3H), 1.58 (*s*, 3H), 1.56 (*s*, 3H)

Isolation of PGC1

Fraction D (0.530 g) which contained one major component was crystallized in hexane-dichloromethane (3:2) upon standing at room temperature to afford **PGC1** (0.500 g) as yellow needles (R$_f$ 0.32, 3% acetone in dichloromethane).

Melting point	196-197°
UV (EtOH) λ_{max} nm (log ε)	362 (4.02), 321 (4.27), 258 (4.43), 242 (4.45), 210 (4.38)
FT-IR (KBr) ν (cm^{-1})	3520 (O-H stretching) 2959, 2907 (C-H stretching) 1635 (C=O stretching)
^{1}H NMR (CDCl$_3$ +DMSO-d_6)(δ ppm)	13.00 (*s*, 1H), 7.30 (*s*, 1H), 6.66 (*s*, 1H), 6.21 (*s*, 1H), 5.04 (*dt*, *J* 7.0, 1.5 Hz, 1H), 4.84 (*br t*, *J* 7.0 Hz, 1H), 3.74 (*s*, 3H), 3.12 (*br d*, *J* 7.0 Hz, 2H), 1.79-1.84 (*m*, 2H), 1.70-1.74 (*m*, 2H), 1.56 (*s*, 3H), 1.40 (*s*, 3H), 1.33(*s*, 3H)

Purification of fraction F

Fraction F (7.108 g) was rechromatographed on column chromatography and eluted with dichloromethane-methanol. The fractions containing similar components were combined into seven fractions (F1-F7).

Isolation of compound PGC10

Fraction F7 (1.15 g) was dissolved in dichloromethane. The soluble fraction (130 mg) was rechromatographed on column chromatography using dichloromethane-methanol as an eluent and further purified by preparative TLC using dichloromethane as an eluent and finally recrystallizied in dichloromethane to afford compound **PGC10** (7.9 mg), as pale yellow solid and **PGC3** (76 mg).

PGC10

Melting point	222-223°
UV (EtOH) λ_{max} nm (log ε)	362 (2.97), 316 (3.27), 235 (3.12)
FT-IR (KBr) ν (cm^{-1})	3408 (O-H stretching) 1654 (C=O stretching)
^{1}H NMR ($CDCl_3$+CD_3COCD_3)(δ ppm)	13.37 (*s*, 1H), 7.58 (*s*, 1H), 6.93 (*s*, 1H), 6.53 (*s*, 1H), 5.34 (*br t*, *J* 7.5 Hz, 1H), 4.32 (*s*, 2H), 4.00 (*s*, 3H), 3.97 (*s*, 3H), 3.42 (*br d*, *J* 8.0 Hz, 2H), 1.76 (*d*, *J* 1.0 Hz, 3H)
^{13}C NMR ($CDCl_3$ CD_3COCD_3)(δ ppm)	180.14, 164.06, 159.55, 156.68, 154.45, 152.98, 146.25, 135.54, 124.85, 113.30, 111.00, 105.21, 103.17, 90.19, 61.29, 56.49, 56.30, 21.61, 21.13

DEPT 135°

CH_3 : 21.61

CH_2 : 21.13

CH : 124.85, 105.21, 103.17, 90.19

Purification of fraction G

Fraction G (12.653 g) was subjected to a quick column chromatography and eluted with dichloromethane-methanol to give seven fractions (G1-G7).

Fraction G5 (45 mg) was rechromatographed on column chromatography and further purified by preparative TLC using dichloromethane as an eluent to give **PGC4** (4.1 mg), **PGC8** (2.0 mg) and **PGC9** (2.0 mg).

Fraction G6 (37 mg) was chromatographed on column chromatography and eluted with hexane-dichloromethane solvent system to afford pure compounds **PGC1** (11.2 mg) and **PGC9** (2.0 mg).

Isolation of PGC 5, PGC 11 and PGC 12

Fraction G7 (0.352 g) was purified by column chromatography and eluted with dichloromethane-methanol to give four fractions. The first fraction (52 mg) was rechromatographed on column chromatography and eluted with dichloromethane-hexane to give pure **PGC11** (4.0 mg) as a yellow solid.

Melting point		92-94°
$[\alpha]_D^{29}$		+40.00° (c = 2.5 x 10^{-3} g/ 10 cm^3, EtOH)
UV (EtOH) λ_{max} nm (log ε)		383 (3.70), 323 (4.32), 265 (4.43), 246 (4.40)
FT-IR (KBr) ν (cm^{-1})		3473 (O-H stretching) 1652 (C=O stretching)
^{1}H NMR ($CDCl_3$)(δ ppm)		13.74 (*s*, 1H), 8.09 (*d*, *J* 10.0 Hz, 1H), 6.83 (*s*, 1H), 6.32 (*s*, 1H), 6.22 (*br s*, 1H), 5.80 (*d*, *J* 10.0 Hz, 1H), 5.30 (*br t*, *J* 7.0 Hz, 1H), 5.10 (*br t*, *J* 7.0 Hz, 1H), 3.46 (*br d*, *J* 7.0 Hz, 2H), 2.09-2.17 (*m*, 2H), 1.85 (*d*, *J* 0.5 Hz, 3H), 1.76-1.82 (*m*, 2H), 1.78 (*d*, *J* 1.0 Hz, 3H), 1.67 (*d*, *J* 1.0 Hz, 3H), 1.58 (*s*, 3H), 1.46 (*s*, 3H)
^{13}C NMR ($CDCl_3$)(δ ppm)		182.55, 161.73, 160.47, 155.34, 153.03, 150.77, 136.82, 135.86, 132.16, 131.45, 123.65, 121.44, 121.39, 119.58, 108.55, 108.36, 103.78, 102.32, 93.42, 79.39, 40.38, 25.86, 25.67, 25.65, 22.77, 21.45, 17.93, 17.67
DEPT 135°	CH_3 :	25.86, 25.67, 25.65, 17.93, 17.67
	CH_2 :	40.38, 22.77, 21.45
	CH :	131.45, 123.65, 121.44, 121.39, 102.32, 93.42

The second fraction (40 mg) was further separated by column chromatography and eluted with dichloromethane to give red-brown viscous liquid. Further purification by preparative TLC using chloroform as an eluent gave **PGC11** (3.5 mg) and **PGC5** (8.6 mg) as yellow solid.

PGC5

Melting piont		201-202°
UV (EtOH) λ_{max} nm (log ε)		362 (2.58), 311 (3.21)
FT-IR (KBr) ν (cm^{-1})		3394 (O-H stretching) 1652 (C=O stretching)
^{1}H NMR ($CDCl_3$ +CD_3COCD_3)(δ ppm)		13.20 (*s*, 1H), 8.86 (*br s*, 1H), 8.24 (*br s*, 1H), 7.75 (*dd*, *J* 8.0, 1.5 Hz, 1H), 7.30 (*dd*, *J* 8.0, 1.5 Hz, 1H), 7.22 (*t*, *J* 8.0 Hz, 1H), 6.55 (*s*, 1H), 5.31 (*dt*, *J* 7.0, 1.5 Hz, 1H), 5.07 (*br t*, *J* 6.5 Hz, 1H), 3.43 (*br d*, *J* 7.0 Hz, 2H), 2.05-2.10 (*m*, 2H), 1.98-2.02 (*m*, 2H), 1.82 (*s*, 3H), 1.64 (*s*, 3H), 1.58 (*s*, 3H)
^{13}C NMR ($CDCl_3$ +CD_3COCD_3)(δ ppm)		180.91, 162.98, 160.76, 155.40, 145.26, 144.93, 136.29, 131.38, 124.34, 123.65, 121.88, 120.12, 116.29, 110.69, 103.27, 93.87, 39.85, 26.69, 25.48, 21.38, 17.67, 16.20
DEPT 135°	CH_3 :	25.48, 17.67, 16.20
	CH_2 :	39.85, 26.69, 21.38
	CH :	124.34, 123.65, 121.88, 120.12, 116.29, 93.8

The third fraction (112 mg) was further purified by preparative TLC using chloroform as an eluent to obtain **PGC5** (9.2 mg) and **PGC12** (38.6 mg), as a red-brown viscous liquid.

UV (EtOH) λ_{max} nm (log ε)	362 (3.57), 312 (4.04), 262 (4.17), 244 (4.24)
FT-IR (KBr) ν (cm^{-1})	3385 (O-H stretching) 1711, 1641 (C=O stretching)

^{1}H NMR ($CDCl_3$)(δ ppm) 13.83 (*s*, 1H), 6.84 (*s*, 1H), 6.35 (*s*, 1H), 5.41 (*dt-like*, *J* 6.0 Hz, 1H), 5.27 (*br t*, *J* 6.5 Hz, 1H), 5.03 (*br t*, *J* 7.0 Hz, 1H), 4.77 (*s*, 2H), 4.11 (*br d*, *J* 5.5 Hz, 2H), 3.81 (*s*, 3H), 3.59 (*dd*, *J* 7.0, 1.0 Hz, 2H), 2.14 (*s*, 3H), 2.03-2.08 (*m*, 2H), 1.90-2.02 (*m*, 2H), 1.83 (*d*, *J* 0.5 Hz, 3H), 1.75 (*d*, *J* 1.0 Hz, 3H), 1.60 (*s*, 3H), 1.55 (*s*, 3H)

^{13}C NMR ($CDCl_3$)(δ ppm) 181.99, 172.17, 161.58, 160.86, 155.86, 155.30, 154.55, 142.64,137.15, 135.57, 131.28, 130.45, 128.63, 124.33, 123.30, 112.27, 108.03, 103.48, 101.60, 93.57, 63.92, 62.06, 39.72, 26.59, 26.53, 25.61, 21.16, 20.99, 20.90, 17.67, 16.50

DEPT 135° CH_3 : 25.61, 21.16, 20.99, 17.67, 16.50
CH_2 : 63.92, 39.72, 26.59, 26.53, 20.90
CH : 128.63, 124.33, 123.30, 101.60, 93.57

2.5 Evaluation of Antioxidation Activity

The potential antioxidation activities of the crude material and pure compounds isolated from the latex of *Garcinia cowa* were assessed on the basis of the scavenging activity of the stable α,α-diphenyl-β-picrylhydrazyl (DPPH) free radical.

2.5.1 Screening on the free radical scavenging activity of the crude material

The crude material was dissolved in absolute ethanol to prepare the solution with the concentration of 3.0 mg/ml. The solution of each sample (50 µl) was mixed with 0.05 mM DPPH ethanolic solution (3 ml) in a cuvette and warm at 37°C.

The trapping effect was assessed by measuring the absorbance change of the solution at 517 nm against 0.05 mM DPPH ethanolic solution every 10 min. The measurements were performed at least in triplicate. The degree of loss of color implied the activity.

Table 3 The average absorption of the solutions (50 μg/ml)

sample	average absorbances (517 nm)				
	0 (min)	10 (min)	20 (min)	30 (min)	40 (min)
DPPH	0.41	0.40	0.40	0.40	0.40
DPPH + crude material	0.34	0.15	0.06	0.04	0.04

2.5.2 Evaluation of IC_{50} value of the crude material

The ethanolic solution of crude material with the concentration of 2.5, 1.25, 0.75, 0.5, 0.25, 0.125, 0.06 and 0.03 mg/ml were prepared. The solution (50 μl) was mixed with the ethanolic solution of DPPH (0.05 mM, 3 ml) to give the solution with the final concentration of 40, 20, 10, 8, 4, 2, 1 and 0.5 μg/ml. The mixed solution was allowed to stand at 37°C for 30 min and the absorbance was measured at 517 nm. BHT was used for a positive control. The measurements were performed at least in triplicate. The results were shown in Table 4. The absorbance at each time point was plotted against the concentration. The concentration that required to scavenge 50% DPPH free radical was the IC_{50}.

IC_{50} (the concentration of the sample at 50% inhibition) was obtained by linear regression analysis of dose response curve, which was plotted between % inhibition and concentration (µg/ml).

$$\% \text{ inhibition} = \frac{A_{\text{control}} - A_{\text{sample}}}{A_{\text{control}}} \times 100$$

Table 4 The average absorption and % inhibition of the sample at various concentrations

concentrations (µg/ml)	crude material		BHT	
	absorbances	% inhibition	absorbances	% inhibition
control (DPPH)	0.40	0	0.40	0
0.5	0.38	5.0	0.36	10.0
1.0	0.36	10.0	0.33	17.5
2.0	0.35	12.5	0.26	35.0
4.0	0.33	17.5	0.22	45.0
8.0	0.27	32.5	0.14	65.0
10.0	0.22	45.0	0.08	80.0
20.0	0.13	67.5	0.05	87.5
40.0	0.04	90.0	0.03	92.5

2.5.3 Free radical scavenging activity of the pure compounds

The testing was performed as in 2.5.2 except the final concentrations of the solution were made at 200 and 100 μM. The results were shown in Table 5.

Table 5 The average absorption and % inhibition of the sample solutions

samples	100 μM		200 μM	
	absorbances	% inhibition	absorbances	% inhibition
control (DPPH)	0.40	0	0.40	0
PGC 1	0.37	7.5	0.33	17.5
PGC 2	0.38	5.0	0.36	10.0
PGC 3	0.36	10.0	0.31	22.5
PGC 4	0.37	7.5	0.34	15.0
PGC 6	0.28	30.0	0.24	40.0
PGC 7	0.32	20.0	0.27	32.5
PGC 12	0.37	7.5	0.35	12.5

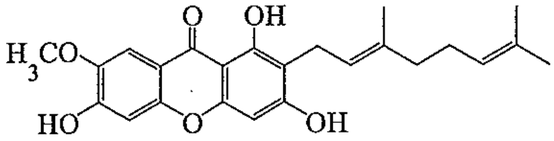
CHAPTER 3

RESULTS AND DISCUSSION

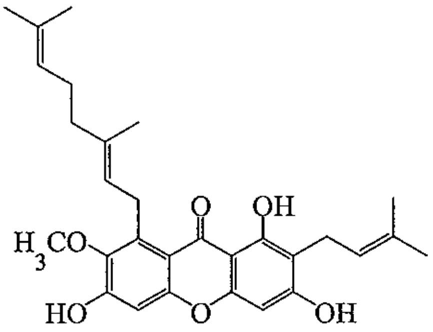
3.1 Structural Determination

The fresh yellowish latex of *Garcinia cowa* collected from Nakhon Sri Tammarat province in the Southern part of Thailand was separated by quick column chromatography over silica gel, eluting with hexane, dichloromethane and acetone in a polarity gradient manner to give nine broad fractions. Selected fractions were further purified by column chromatography, preparative TLC and / or crystallization to afford seven new xanthones **(PGC6-12)** and five previously reported xanthones: cowaxanthone **(PGC1)**, cowanin **(PGC2)**, cowanol **(PGC3)**, 1,3,6-trihydroxy-7-methoxy-2,5-bis(3-methylbut-2-enyl)xanthone **(PGC4)** and mangostinone **(PGC5)**. The structures were elucidated by spectroscopic methods.

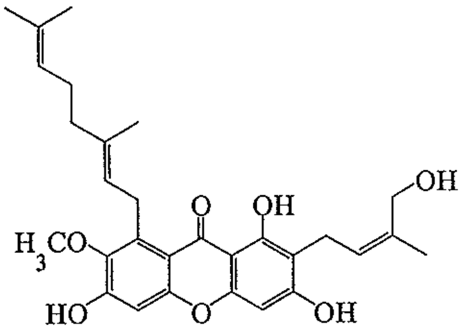
The structure of compounds isolated from the latex of *Garcinia cowa*



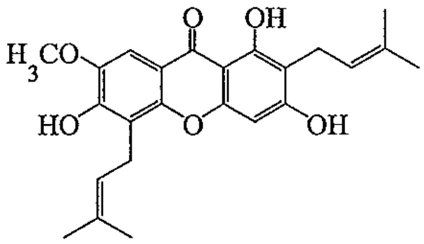
cowaxanthone (**PGC1**)



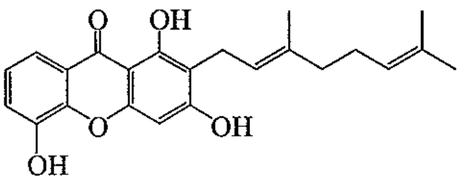
cowanin (**PGC2**)



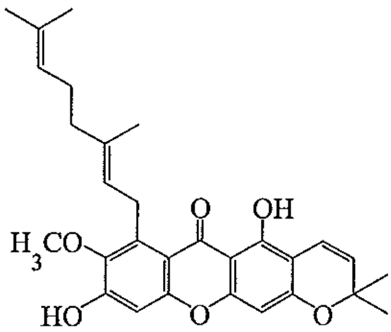
cowanol (**PGC3**)



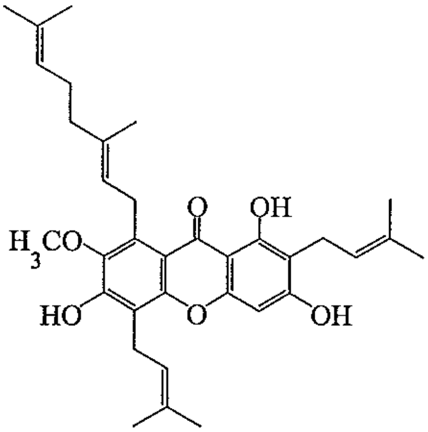
1,3,6-trihydroxy-7-methoxy-2,5-bis (3-methyl-2-butenyl)xanthone (**PGC4**)



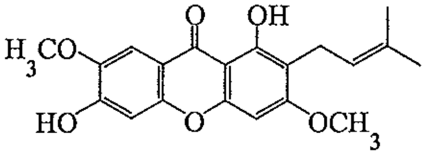
mangostinone (**PGC5**)



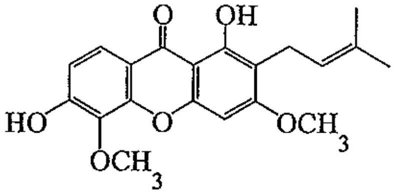
PGC6



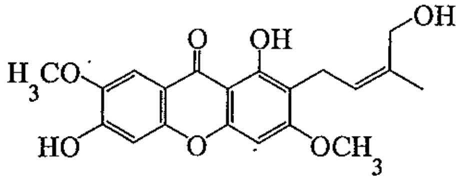
PGC7



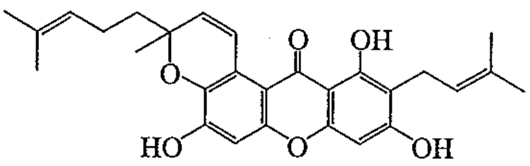
PGC8



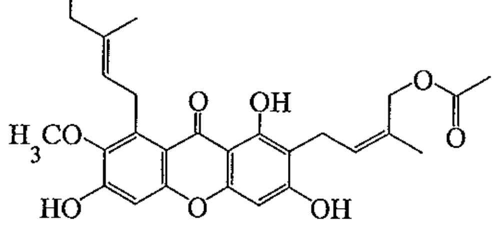
PGC9



PGC10

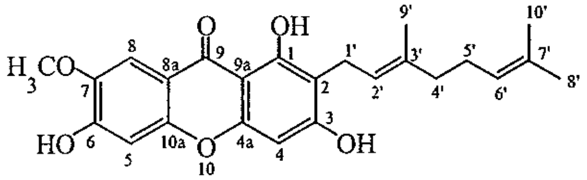


PGC11



PGC12

3.1.1 PGC1: 1,3,6-trihydroxy-7-methoxy-2-(3,7-dimethyl-2,6-octadienyl)xanthone (cowaxanthone)



PGC1 is a glisten yellow crystal, m.p. 196-197°. The UV spectrum showed maximum absorption bands at 362, 321, 258, 242 and 210 nm. The IR spectrum showed the broad absorption band of O-H stretching at 3520 cm^{-1} and the sharp band of C=O stretching at 1635 cm^{-1}. The ^1H NMR spectrum exhibited a sharp singlet signal of a chelated hydroxy proton C1-OH at δ 13.00 and three singlet signals of three isolated aromatic protons at δ 7.30, 6.66 and 6.21. The most deshielded aromatic proton signal, δ 7.30, was assigned for a signal of H-8 according to an anisotropic effect by the carbonyl group. The other two aromatic proton signals, δ 6.66 and 6.21, were assigned for H-5 and H-4, respectively. The sharp singlet resonance at δ 3.74 belonged to the methoxy group and it was located at C-7. The remaining proton signals were assigned for geranyl side chain which was located at C-2. Those signals were assigned as follow; three singlet signals at δ 1.56, 1.40 and 1.33 were of three vinylic methyl groups, a doublet signal at δ 3.12 was assigned for benzylic methylene protons H-1′, two sets of multiplet signals at δ 1.79-1.84 and 1.70-1.74 were the signals of two groups of methylene protons H-5′ and H-4′ and two sets of broad triplet signals at δ 5.04 and 4.84 were the signals of two olefinic methine protons H-2′ and H-6′. The result of the decoupling experiment by irradiation at the resonance of methylene proton H-1′ (δ 3.12) effected the olefinic methine proton H-2′ (δ 5.04) whereas irradiation at the resonance of methylene proton H-5′ (δ 1.79-1.84) resulted in the collapsion of the

resonance of methylene proton H-4′ (δ 1.70-1.74) and olefinic methine proton H-6′ (δ4.84), thus the side chain was confirmed to be geranyl group. Therefore the structure of **PGC1** was assigned to be 1,3,6-trihydroxy-7-methoxy-2-(3,7-dimethyl-2,6-octadienyl)xanthone. The proposed structure, the spectral data and the melting point were found to be corresponded to the previously isolated compound, cowaxanthone (Likhitwitayawuid, *et al.*, 1997).

Table 6 The ^{1}H NMR spectral data of **PGC1**

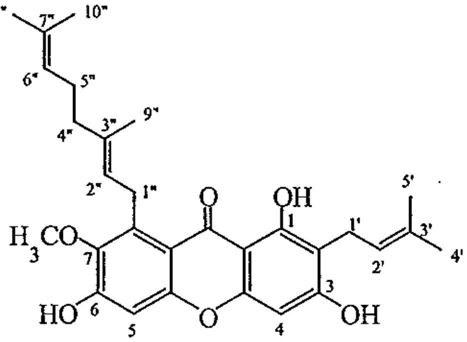
Position	**PGC1** δ_H (*multiplicity*, J_{Hz})	^{A}cowaxanthone δ_H (*multiplicity*, J_{Hz})
1	13.00 (*s*, 1H)	14.34 (*s*, 1H)
2	-	-
3	-	10.82 (*br s*, 1H)
4	6.21 (*s*, 1H)	6.39 (*s*, 1H)
5	6.66 (*s*, 1H)	6.87 (*s*, 1H)
6	-	10.82 (*br s*, OH)
7	-	-
7-OCH_3	3.74 (*s*, 3H)	3.86 (*s*, 3H)
8	7.30 (*s*, 1H)	7.41 (*s*, 1H)
1′	3.12 (*br d*, 7.0 Hz, 2H)	3.21 (*br d*, 2H, 7.0 Hz)
2′	5.04 (*br t*, 7.0 Hz, 1H)	5.17 (*br t*, 1H, 7.0 Hz)
3′	-	-

Table 6 (Continued)

Position	**PGC1** δ_H (*multiplicity*, J_{Hz})	^{A}cowaxanthone δ_H (*multiplicity*, J_{Hz})
4′	1.70-1.74 (*m*, 2H)	1.89 (*m*, 2H)
5′	1.79-1.84 (*m*, 2H)	1.98 (*m*, 2H)
6′	4.84 (*br t*, 7.0 Hz, 1H)	5.01 (*br t*, 7.0 Hz, 1H)
7′	-	-
8′	1.33 (*s*, 3H)	1.49 (*s*, 3H)
9′	1.56 (*s*, 3H)	1.71 (*s*, 3H)
10′	1.40 (*s*, 3H)	1.55 (*s*, 3H)

^{A}300 MHz, in DMSO-d_6

3.1.2 PGC2: 1,3,6-trihydroxy-7-methoxy-2-(3-methyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl)xanthone (cowanin)



PGC2 is a yellow solid, m.p. 136-137°. The UV spectrum showed maximum absorption bands at 355, 316, 255, 242 and 212 nm. The IR spectrum showed the absorption bands of conjugated carbonyl group at 1636 cm^{-1} and hydroxy group at 3425 cm^{-1}. The ^{1}H NMR spectrum exhibited a resonance of a chelated hydroxy group 1-OH at δ13.70. Two singlets in aromatic region, δ6.83 and 6.30 were assigned to be the signals of isolated proton H-5 and H-4, respectively. The presence of a methoxy group was shown at δ3.80 as a singlet resonance and its was located at C-7. The ^{1}H NMR spectrum further revealed a characteristic signal of a prenyl unit, of which the signal of *gem*-dimethyl protons resonated as two singlets at δ1.82 and 1.77, a doublet due to benzylic methylene protons H-1′ were at δ3.45 and a broad triplet of an olefinic methine proton H-2′ was at δ5.29. On decoupling experiment the benzylic methylene protons H-1′ and olefinic methine proton H-2′ were found to couple to each other. The remaining signals were assigned for geranyl group. A doublet signal at δ4.10 and a broad triplet signal at δ5.26 were assigned for the signals of methylene protons H-1″ and an olefinic proton H-2″, respectively. A broad triplet signal at δ5.03 and two multiplets at δ1.97-2.00 and 2.02-2.07 were the signals of an olefinic proton H-6″ and

two groups of methylene proton H-4″ and H-5″, respectively. Three singlet signals at δ 1.84, 1.59 and 1.54 were those of three methyl groups. These assignments were confirmed by decoupling experiment. Since the chemical shift of methylene protons H-1″of geranyl side chain was appeared at the lower field than H-1′of isoprenyl side chain, the geranyl group thus was placed nearby the carbonyl group and the isoprenyl moiety was placed at C-2. Therefore **PGC2** was assigned to be 1,3,6-trihydroxy-7-methoxy-2-(3-methylbut-2-enyl)-8-(3,7-dimethyl-2,6-octadienyl)xanthone. The proposed structure, the spectral data and melting point were agreed with the structure of cowanin (Na Pattalung, *et al.*, 1994).

Table 7 The ^{1}H NMR spectral data of **PGC2**

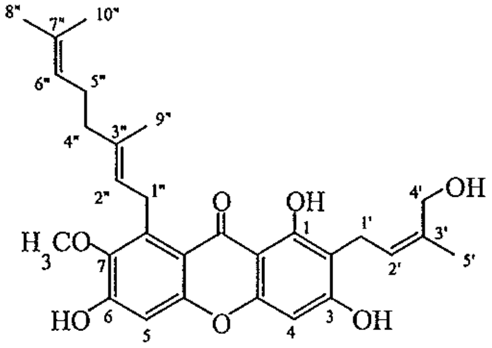
Position	**PGC2** δ_H (*multiplicity*, J_{Hz})	^{A}cowanin δ_H (*multiplicity*, J_{Hz})
1	13.70 (*s*, OH)	13.80 (*s*, OH)
2	-	-
3	-	-
4	6.30 (*s*, 1H)	6.30 (*s*, 1H)
5	6.83 (*s*, 1H)	6.86 (*s*, 1H)
6	-	-
7	-	-
7-OCH_3	3.80 (*s*, 3H)	3.80 (*s*, 3H)
8	-	-
1′	3.45 (*br d*, 7.0 Hz, 2H)	3.45 (*br d*, 7.0 Hz, 2H)
2′	5.29 (*br t*, 7.0Hz, 1H)	5.28 (*br t*, 7.0 Hz, 1H)
3′	-	-

Table 7 (Continued)

Position	**PGC2** δ_H (*multiplicity*, J_{Hz})	^{A}cowanin δ_H (*multiplicity*, J_{Hz})
4′	1.77 (*s*, 3H)	1.76 (*s*, 3H)
5′	1.82 (*s*, 3H)	1.82 (*s*, 3H)
1″	4.10 (*br d*, 7.0 Hz, 2H)	4.09 (*br d*, 7.0 Hz, 2H)
2″	5.26 (*br t*, 7.0 Hz, 1H)	5.28 (*br t*, 7.0 Hz, 1H)
3″	-	-
4″	1.97-2.00 (*m*, 2H)	2.03 (*m*, 2H)
5″	2.02-2.07 (*m*, 2H)	2.03 (*m*, 2H)
6″	5.03 (*br t*, 6.5 Hz, 1H)	5.03 (*br t*, 1H)
7″	-	-
8″	1.54 (*s*, 3H)	1.59 (*s*, 3H)
9″	1.84 (*s*, 3H)	1.84 (*s*, 3H)
10″	1.59 (*s*, 3H)	1.61 (*s*, 3H)

^{A}400 MHz, in $CDCl_3$

3.1.3 PGC3: 1,3,6-trihydroxy-7-methoxy-2-(3-methylbut-4-hydroxy-2-enyl)-8-(3,7-dimethyl-2,6-octadienyl)xanthone (cowanol)



PGC3 is a pale-yellow solid, m.p. 123-124°. The UV spectrum showed maximum absorption bands at 355, 316, 255, 244 and 212 nm. The IR spectrum showed the sharp absorption band of conjugated carbonyl group at 1646 cm^{-1} and the broad band of hydroxy group at 3365 cm^{-1}. The ^{1}H NMR spectrum revealed a signal for hydrogen bonded hydroxy function at δ13.83. In the aromatic region, two singlet resonances at δ6.85 and 6.32 were assigned for the resonances of H-5 and H-4, respectively. A sharp singlet signal at δ3.82 due to the signal of the protons of methoxy group at C-7. The resonances of geranyl side chain were present in the spectrum. In comparison to the spectrum of compound **PGC1** and **PGC2**, the signals of geranyl side chain were assigned as follow; a doublet at δ4.12 and a doublet of triplet at δ5.28 were the signals of a methylene protons H-1$''$ and an olefinic proton H-2$''$, a broad triplet at δ5.04 and two sets of multiplet signals at δ2.00-2.03 and 2.04-2.08 belonged to an olefinic proton H-6$''$ and two groups of methylene protons H-4$''$ and H-5$''$, respectively and three singlets at δ1.84, 1.61 and 1.56 were the resonances of three methyl groups. The remaining resonances appearing as a doublet of triplet at δ5.48, a doublet at δ3.54, a singlet with two protons at δ4.37 and a singlet at δ1.79 were

assigned for olefinic proton H-2′, benzylic methylene protons H-1′, oxymethylene protons H-4′ and methyl protons H-5′, respectively. The evidence suggested that the structure contained the 4-hydroxy-3-methyl-2-butenyl as a side chain. Since the chemical shift of the methylene protons of geranyl side chain (H-1″, δ 3.62) was at the lower field than the methylene protons (H-1′, δ 3.49) of 4-hydroxy-3-methyl-2-butenyl side chain, thus the geranyl was proposed to be nearby the carbonyl group and the 4-hydroxy-3-methyl-2-butenyl side chain was located at C-2. The proposed structure of **PGC3** was 1,3,6-trihydroxy-7-methoxy-2-(3-methyl-4-hydroxy-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl)xanthone. The proposed structure, the spectral data and melting point was corresponded to cowanol (Na Pattalung, *et al.*, 1994).

Table 8 The ^{1}H NMR spectral data of **PGC3**

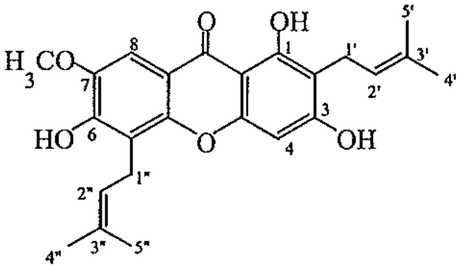
Position	**PGC3** δ_H (*multiplicity*, J_{Hz})	^{A}cowanol δ_H (*multiplicity*, J_{Hz})
1	13.83 (*s*, OH)	13.96 (*s*, OH)
2	-	-
3	-	-
4	6.32 (*s*, 1H)	6.28 (*s*, 1H)
5	6.85 (*s*, 1H)	6.80 (*s*, 1H)
6	-	-
7	-	-
7-OCH$_3$	3.82 (*s*, 3H)	3.79 (*s*, 3H)
8	-	-

Table 8 (Continued)

Position	**PGC3** δ_H (*multiplicity*, J_{Hz})	[A]cowanol δ_H (*multiplicity*, J_{Hz})
1′	3.54 (*br d*, 7.0 Hz, 2H)	3.51 (*br d*, 7.0 Hz, 2H)
2′	5.48 (*dt*, 7.0, 1.5 Hz, 1H)	5.47 (*br t*, 7.0 Hz ,1H)
3′	-	-
4′	4.37 (*s*, 2H)	4.35 (*br s*, 2H)
5′	1.79 (*s*, 3H)	1.79 (*s*, 3H)
1″	4.12 (*br d*, 7.0 Hz, 2H)	4.09 (*br d*, 7.0 Hz, 2H)
2″	5.28 (*dt*, 7.0, 1.5 Hz, 1H)	5.24 (*br t*, 7.0 Hz, 1H)
3″	-	-
4″	2.00-2.03 (*m*, 2H)	2.03 (*m*, 2H)
5″	2.04-2.08 (*m*, 2H)	2.03 (*m*, 2H)
6″	5.04 (*br t*, 7.0Hz, 1H)	5.02 (*br t*, 7.0 Hz, 1H)
7″	-	-
8″	1.56 (*s*, 3H)	1.54 (*s*, 3H)
9″	1.84 (*s*, 3H)	1.82 (*s*, 3H)
10″	1.61 (*s*, 3H)	1.59 (*s*, 3H)

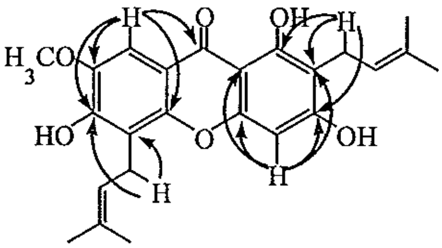
[A]400 MHz, in $CDCl_3$

3.1.4 PGC4: 1,3,6-trihydroxy-7-methoxy-2, 5-bis (3-methyl-2-butenyl)xanthone



PGC4 is a pale-yellow solid, m.p. 222-224°. The UV spectrum showed maximum absorption bands at 362, 318, 259 and 240 nm. The IR spectrum showed the absorption bands of hydroxy group at 3382 cm^{-1} and conjugated carbonyl group at 1646 cm^{-1}. The presence of the carbonyl functionality was confirmed by the signal at δ180.31 in the ^{13}C NMR spectrum. The ^{1}H NMR spectrum exhibited a sharp singlet signal of a hydroxy proton which formed intramolecular hydrogen bond to a carbonyl group at δ 13.48. In addition, two broad singlet signals of two more hydroxy protons were observed at δ6.44 and 6.21. These three signals were confirmed to be the signals of hydroxy groups on addition of D_2O. Two sharp singlet signals in aromatic region, δ7.51 and δ6.43 were assigned to be the isolated aromatic protons H-8 and H-4, respectively. Proton H-8 (δ 7.51) was found on the NOE experiment to effect a methoxy group which exhibited the signal at δ4.00. Subsequently, the methoxy group was assigned to be at C-7. Two sets of signal that were suggestive to be signals of two isoprenyl groups were displayed. Those signals were two broad triplet signals of two olefinic protons at δ5.31 (H-2′) and 5.29 (H-2″), two doublet signals of benzylic methylene protons at δ3.49 (H-1′) and 3.62 (H-1″) and four singlet signals of four methyl groups at δ1.86, 1.79, 1.88 and 1.69. HMBC correlations of methylene protons H-1′ (δ3.49) to C-1, C-2 and C-3 and methylene proton H-1″(δ3.62) to C-5 and C-6 indicated that the isoprenyl side chain were at C-2 and C-5. The assignment of

aromatic proton H-4 was confirmed by the correlations of H-4 (δ 6.43) to C-2, C-3, C-4a and C-9a whereas the position of aromatic proton H-8 was proved by the correlations of H-8 (δ7.51) to C-6, C-7, C-9 and C-10a. The ^{13}C NMR spectrum and DEPT experiments (Table 9) indicated the presence of a carbonyl carbon (δ 180.31), four methyl carbons (δ25.82, 25.74 and 17.93 x2), two methylene carbons (δ22.39 and 21.44), four methine carbons (δ 121.33, 120.90, 101.99 and 94.07), a methoxy carbon (δ 56.40) and twelve quaternary carbons (δ 161.84, 160.15, 156.02, 150.74, 149.93, 143.98, 136.01, 132.76, 115.47, 113.01, 108.44 and 101.99).



Major HMBC of **PGC4**

These assignment indicated that **PGC4** was 1,3,6-trihydroxy-7-methoxy-2,5-bis (3-methyl-2-butenyl)xanthone. The structure of **PGC4** and its melting point were identical to the previously isolated compound of Na Pattalung (Na Pattalung, *et al.*, 1994).

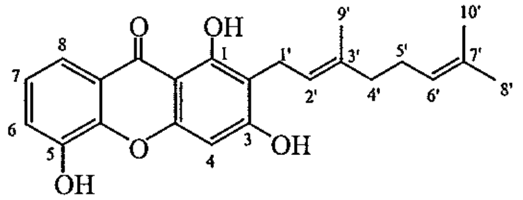
Table 9 The NMR spectral data of **PGC4**

Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
1	160.15 (C)	13.48 (*s*, OH)	C-1, C-2, C-9a
2	108.44 (C)	-	-

Table 9 (Continued)

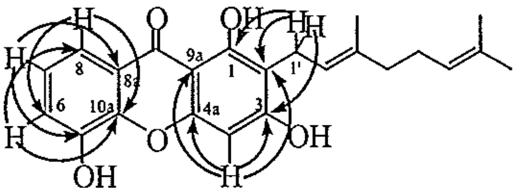
Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
3	161.84 (C)	6.21 (*s*, OH)	C-2, C-3, C-4
4	94.07 (CH)	6.43 (*s*, 1H)	C-2, C-3, C-4a, C-9a
4a	156.02 (C)	-	-
5	115.47 (C)	-	-
6	150.47 (C)	6.44 (*s*, OH)	C-5, C-6, C-7
7	143.98 (C)	-	-
7-OCH_3	56.40 (OCH_3)	4.00 (*s*, 3H)	C-7
8	101.99 (CH)	7.51 (*s*, 1H)	C-6, C-7, C-9, C-10a
8a	113.01 (C)	-	-
9	180.31 (C=O)	-	-
9a	101.99 (C)	-	-
10a	149.93 (C)	-	-
1′	21.44 (CH_2)	3.49 (*br d*, 7.5 Hz, 2H)	C-1, C-2, C-3, C-12, C-13
2′	121.33 (CH)	5.31 (*br t*, 7.5 Hz, 1H)	-
3′	136.01 (C)	-	-
4′	25.82 (CH_3)	1.79 (*s*, 3H)	C-12, C-13, C-15
5′	17.93 (CH_3)	1.86 (*s*, 3H)	C-12, C-13, C-14
1″	22.39 (CH_2)	3.62 (*br d*, 7.5 Hz, 2H)	C-5, C-6
2″	120.90 (CH)	5.29 (*br t*, 7.0Hz, 1H)	-
3″	132.76 (C)	-	-
4″	25.74 (CH_3)	1.69 (*s*, 3H)	C-17, C-18, C-20
5″	17.93 (CH_3)	1.88 (*s*, 3H)	C-17, C-18, C-19

3.1.5 PGC5: 1,3,5-trihydroxy-2-(3,7-dimethyl-2,6-octadienyl)xanthone (mangostinone)



PGC5 was obtained as a yellow solid, m.p. 201-202°. The UV spectrum showed maximum absorption bands at 362 and 311 nm. The IR spectrum showed the absorption bands of conjugated carbonyl group at 1652 cm^{-1} and hydroxy group at 3394 cm^{-1}. The ^{1}H NMR spectrum exhibited the singlet signals of a chelated hydroxy group at δ13.20 and two phenolic hydroxy groups at δ8.86 and 8.24. These signals were confirmed to be the signal of hydroxy group upon the disappearance on D_2O exchange. A singlet signal of aromatic proton, δ6.55, was observed and was assigned for the signal of H-4 according to the correlations to C-2, C-3, C-4a and C-9a on the HMBC experiment. The ABM pattern in aromatic region, δ7.75 (*dd*), 7.30 (*dd*) and 7.22 (*t*) were present in the spectrum and were proposed for the characteristic signals of H-8, H-6 and H-7, respectively. The most deshielded aromatic proton signal was assigned for H-8 according to an anisotropic effect of the carbonyl group. The assignment of three aromatic protons H-8, H-6 and H-7 were supported by ^3J coupling of H-8 to C-6 and C-10a; H-7 to C-5 and C-8a; and H-6 to C-8 and C-10a on HMBC experiment. The remaining signals which were three methyl group signals at δ1.82 (H-9′), 1.64 (H-8′) and 1.58 (H-10′), three methylene proton signals at δ3.43 (H-1′), 1.98-2.02 (H-4′) and 2.05-2.10 (H-5′), and two olefinic methine protons signals at δ5.31 (H-2′) and 5.07 (H-6′) appeared as a typical signal of a geranyl moiety. This side chain was located at C-2 according to NOE experiment of which irradiation of

benzylic methylene protons H-1′ (δ 3.43) gave the enhancement to the signal of chelated hydroxy proton at C-1. In addition the correlations of H-1′(δ3.43) to C-1, C-2 and C-3 on 2D HMBC supported the location of geranyl side chain to be at C-2.



Major HMBC of **PGC5**

The ^{13}C NMR spectral data (Table 10) deduced from DEPT and HMQC spectra showed 22 signals for 23 carbon atoms: a carbonyl carbon (δ 180.91), three methyl carbons (δ 25.48, 17.67 and 16.20), three methylene carbons (δ 39.85, 26.69 and 21.38), six methine carbons (δ 124.34, 123.65, 121.88, 120.12, 116.29 and 93.87) and ten quaternary carbons (δ 162.98, 160.76, 155.40, 145.26, 144.93, 136.29, 131.38, 121.88, 110.69 and 103.27). **PGC5** was then identified to be 1,3,5-trihydroxy-2-(3,7-dimethyl-2,6-octadienyl)xanthone. It was the first reported xanthone in *G. cowa*. Its physical and spectral data were in agreement with mangostinone which was previously isolated from *G. mangostana* (Asai, *et al.*, 1995).

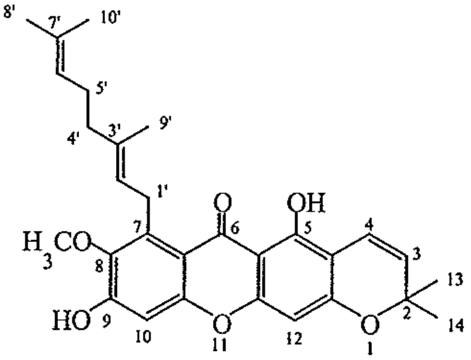
Table 10 The NMR spectral data of **PGC5**

Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
1	160.76 (C)	13.20 (*s*, OH)	C-1, C-2, C-9a
2	110.69 (C)	-	-
3	162.98 (C)	8.86 (*br s*, OH)	C-2, C-3, C-4

Table 10 (Continued)

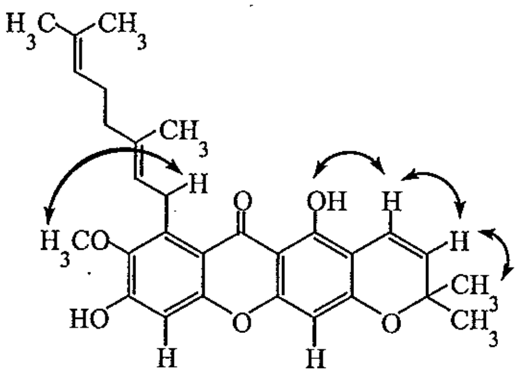
Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
4	93.87 (CH)	6.55 (*s*, 1H)	C-2, C-3, C-4a, C-9a
4a	155.40 (C)	-	-
5	145.26 (C)	8.24 (*br s*, OH)	C-6
6	120.12 (CH)	7.30 (*dd*, 8.0, 1.5 Hz, 1H)	C-8, C-10a
7	123.65 (CH)	7.22 (*t*, 8.0 Hz, 1H)	C-5, C-8a
8	116.29 (CH)	7.75 (*dd*, 8.0, 1.5 Hz, 1H)	C-6, C-10a
8a	121.88 (C)	-	-
9	180.91 (C=O)	-	-
9a	103.27 (C)	-	-
10a	144.93 (C)	-	-
1′	21.38 (CH_2)	3.43 (*br d*, 7.0 Hz, 2H)	C-1, C-2, C-3, C-12, C-13, C-19
2′	121.88 (CH)	5.31 (*dt*, 7.0, 1.5 Hz, 1H)	C-11, C-14, C-19
3′	136.29 (C)	-	-
4′	39.85 (CH_2)	1.98-2.02 (*m*, 2H)	C-12, C-13, C-15
5′	26.69 (CH_2)	2.05-2.10 (*m*, 2H)	C-14, C-16, C-17
6′	124.34 (CH)	5.07 (*br t*, 6.5 Hz, 1H)	C-15, C-20
7′	131.38 (C)	-	-
8′	25.48 (CH_3)	1.64 (*s*, 3H)	C-16, C-17, C-20
9′	16.20 (CH_3)	1.82 (*s*, 3H)	C-12, C-13, C-14
10′	17.67 (CH_3)	1.58 (*s*, 3H)	C-16, C-17, C-18

3.1.6 PGC6: 5,9-dihydroxy-8-methoxy-2,2-dimethyl-7-(3,7-dimethyl-2,6-octadienyl)-*2H,6H*-pyrano[3,2-*b*]xanthen-6-one

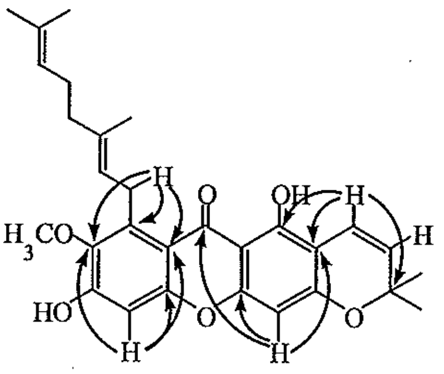


PGC6 is a yellow viscous liquid. The UV spectrum showed maximum absorption bands at 331, 290 and 238 nm. The IR spectrum showed absorption bands of the hydroxy group at 3404 cm^{-1} and the conjugated carbonyl group at 1648 cm^{-1}. The ^1H NMR spectrum (Table 11) exhibited a signal of hydrogen bonded hydroxy function at δ13.74. Two singlet signals in aromatic region, δ6.83 and 6.24 were observed and assigned to be the signals of aromatic proton H-10 and H-12. A sharp singlet signal with three protons at δ3.80 was the signal of methoxy group at C-8. The ^1H NMR spectrum revealed a characteristic signal of a dimethylchromene ring, of which the signal of *gem*-dimethyl protons resonated as a singlet at δ1.47 and two doublet signals of two *cis*-olefinic protons (H-4 and H-3) were at δ6.73 and 5.57. Irradiation of the proton (H-4) at δ6.73 caused an NOE enhancement of the chelated hydroxy group at 5-OH, this suggested that dimethylchromene ring was fused in a linear fashion to the xanthone nucleus. The correlation of H-4 to C-4a and C-5 precisely determined that dimethylchromene ring was next to C-5. In addition, the signals of three methyl groups at δ 1.83 (H-9′), 1.60 (H-8′) and 1.55 (H-10′), three methylene protons at δ 4.09 (H-1′), 2.03-2.07 (H-5′) and 2.00-2.02 (H-4′), and two olefinic methine protons at

δ5.27 (H-2′) and 5.03 (H-6′) which were a characteristic signals of a geranyl moiety were present in the spectrum. The chemical shift of the methylene protons H-1′ (δ4.09) implied that H-1′ was deshielded by a carbonyl group, accordingly the geranyl side chain was proposed to be at C-7, a *peri* position to the carbonyl group. The HMBC correlation of H-1′ to C-6a, C-7 and C-8 confirmed the presence of the geranyl unit at C-7. In addition, the enhancement of benzylic methylene protons (H-1′) upon irradiation at C8-OCH$_3$ (δ3.80) supported the assignment of the methoxy group and the geranyl unit. Aromatic protons H-10 and H-12 were confirmed by the cross peak of H-10 to C-6a, C-8 and C-10a and cross peaks of H-12 to C-4a, C-5, C-6 and C-11a. The ^{13}C NMR spectral data (Table 11) deduced from DEPT and HMQC spectra showed 28 signals for 29 carbon atoms: a carbonyl carbon (δ 181.93), five methyl carbons (δ28.30, 25.63, 17.67 and 16.49), three methylene carbons (δ39.71, 26.55 and 26.48), six methine carbons (δ127.12, 124.28, 123.20, 115.72, 101.66 and 94.15), a methoxy carbon (δ62.02) and thirteen quaternary carbons (δ159.83, 157.91, 156.24, 155.70, 154.58, 142.69, 137.07, 135.61, 131.29, 112.18, 104.48, 103.70 and 77.92).



NOE of **PGC6**



Major HMBC of **PGC6**

According to the assignment, **PGC6** was 5,9-dihydroxy-8-methoxy-2,2-dimethyl-7-(3,7-dimethyl-2,6-octadienyl)-*2H,6H* -pyrano[3,2-*b*]xanthen-6-one. It was a new naturally occurring xanthone.

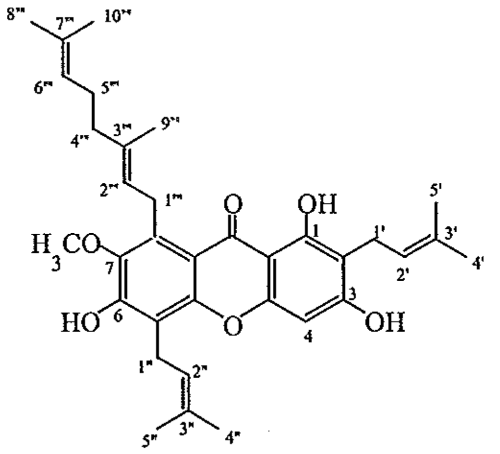
Table 11 The NMR spectral data of **PGC6**

Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
2	77.92 (C)	-	-
13	28.30 (2xCH_3)	1.47 (*s*, 2x3H)	C-2, C-3, C-4
3	127.12 (CH)	5.57 (*d*, 10.0 Hz, 1H)	C-2, C-4a, C-13
4	115.72 (CH)	6.73 (*dd*, 10.0, 0.5 Hz, 1H)	C-2, C-4a, C-5
4a	104.48 (C)	-	-
5	159.83 (C)	13.74 (*s*, OH)	C-4a, C-12a
5a	103.70 (C)	-	-
6	181.93 (C=O)	-	-
6a	112.18 (C)	-	-
7	137.07 (C)	-	-
8	142.69 (C)	-	-
8-OCH_3	62.02 (OCH_3)	3.80 (*s*, 3H)	C-8
9	154.58 (C)	-	-
10	101.66 (CH)	6.83 (*s*, 1H)	C-6, C-6a, C-8, C-10a
10a	155.70 (C)	-	-
11a	156.24 (C)	-	-
12	94.15 (CH)	6.24 (*s*, 1H)	C-4a, C-5, C-6, C-11a
12a	157.91 (C)	-	-

Table 11 (Continued)

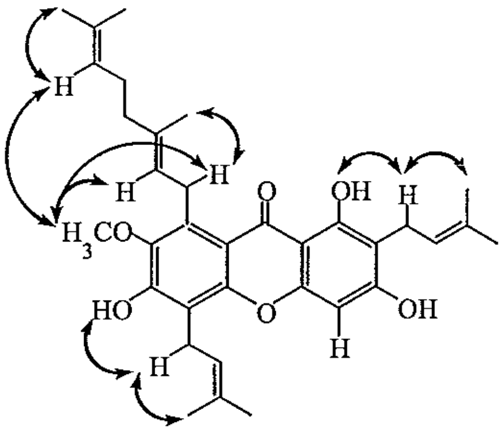
Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
1′	26.55 (CH_2)	4.09 (*br d*, 6.0 Hz, 2H)	C-6a, C-7, C-8, C-2′, C-3′, C-4′, C-9′
2′	123.20 (CH)	5.27 (*dt*, 6.5, 1.5 Hz, 1H)	C-7, C-1′, C-4′, C-9′
3′	135.61 (C)	-	-
4′	39.74 (CH_2)	2.00-2.02 (*m*, 2H)	C-1′, C-2′, C-3′, C-9′
5′	26.48 (CH_2)	2.03-2.07 (*m*, 2H)	C-3′, C-4′, C-6′, C-7′
6′	124.28 (CH)	5.03 (*br t*, 6.5 Hz, 1H)	C-4′, C-9′, C-10′
7′	131.29 (C)	-	-
8′	25.63 (CH_3)	1.60 (*d*, 0.5 Hz, 3H)	C-4′, C-6′, C-7′, C-10′
9′	16.49 (CH_3)	1.83 (*d*, 0.5 Hz, 3H)	C-2′, C-3′, C-4′
10′	17.67 (CH_3)	1.55 (*s*, 3H)	C-6′, C-7′, C-8′

3.1.7 PGC7: 1,3,6-trihydroxy-7-methoxy-2,5-bis(3-methyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl) xanthone

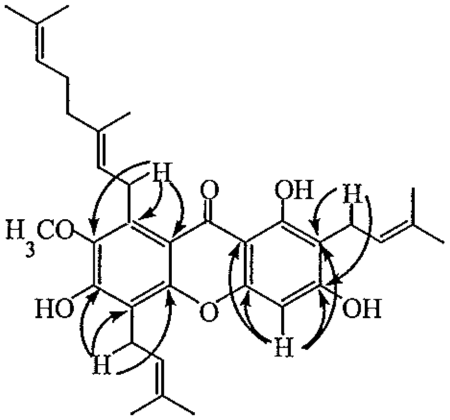


PGC7 is a yellow viscous liquid. The UV spectrum showed maximum absorption bands at 362, 315 and 246 nm. The IR spectrum showed the absorption bands of hydroxy group at 3418 cm^{-1} and conjugated carbonyl group at 1641 cm^{-1}. The ^{1}H NMR spectrum (Table 12) showed a sharp singlet signal of a chelated hydroxy group C1-OH at δ13.89 and a broad singlet signal of free hydroxy group at δ6.45. These signals were supported to be the signals of hydroxy proton by signal disappearance upon addition of D$_2$O. The singlet resonance of an aromatic proton and a singlet signal of methoxy protons were exhibited at δ 6.34 and at δ 3.80, respectively. The characteristic resonances of a geranyl unit were observed. Those signals were a doublet of methylene protons H-1‴ at δ4.08, a broad triplet of olefinic proton H-2‴ at δ5.27, a broad triplet of olefinic proton H-6‴ at δ5.03, two multiplet signals of methylene protons H-4‴ and H-5‴ at δ1.90-2.02 and 2.03-2.08 and three doublets of three methyl groups H-9‴, H-8‴ and H-10‴ at δ1.83, 1.60 and 1.55.

The enhancement of H-1‴ (δ4.08) by irradiation at the resonance of methoxy proton (δ3.80) suggested that the geranyl group was at the *ortho* position to the methoxy group. The remaining signals appeared as typical signals of two isoprenyl units. The signals of the first isoprenyl unit consisted of two doublets of *gem*-dimethyl protons H-4′ and H-5′at δ1.78 and 1.85, a broad triplet of olefinic proton H-2′ at δ5.31 and a doublet of benzylic methylene protons H-1′ at δ3.46. The signals of the second isoprenyl unit consisted of two doublet signals of *gem*-dimethyl protons H-4″ and H-5″ at δ1.88 and 1.69, a broad triplet of olefinic proton H-2″ at δ5.29 and a doublet of benzylic methylene protons H-1″ at δ3.57. The ^{13}C NMR spectral data (Table 12) deduced from DEPT and HMQC spectra showed 34 signals for 34 carbon atoms: a carbonyl carbon (δ182.38), seven methyl carbons (δ25.86, 25.80, 25.62, 17.97, 17.93, 17.67 and 16.46), five methylene carbons (δ39.72, 26.57, 26.34, 22.64 and 21.22), five methine carbons (δ124.32, 123.59, 121.54, 121.14 and 93.23), a methoxy carbon (δ62.02) and fifteen quaternary carbons (δ161.51, 160.56, 155.04, 153.52, 152.28, 142.28, 135.67, 135.29, 133.90, 132.67, 131.26, 113.93, 111.96, 108.35 and 103.56). The assignments of the substituted group were deduced from HMQC experiment. Aromatic proton (δ6.34) was suggested to H-4 from the cross peak of H-4 to C-2, C-3, C-4a and C-9a. The methoxy group (δ3.80) was indicated to be at C-7 from the ^3J coupling of methoxy protons to C-7. The geranyl unit was located at C-8 according to the correlations of benzylic methylene protons H-1‴ (δ4.09) to C-7, C-8 and C-8a. The methylene protons H-1′ (δ3.46) were found to correlate to C-2 and C-3 whereas the methylene protons H-1″ (δ3.57) correlated to C-5, C-6 and C-10a, consequently, two isoprenyl units were determined to be at C-2 and C-5, respectively.



NOE of **PGC7**



Major HMBC of **PGC7**

The elucidation revealed that **PGC7** was 1,3,6-trihydroxy-7-methoxy-2,5-bis (3-methyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl)xanthone. This compound was a new naturally occurring xanthone.

Table 12 The NMR spectral data of **PGC7**

Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
1	160.56 (C)	13.89 (*s*, OH)	C-1, C-2, C-9a
2	108.35 (C)	-	-
3	161.51 (C)	-	-
4	93.23 (CH)	6.34 (*s*, 1H)	C-2, C-3, C-4a, C-9, C-9a
4a	155.04 (C)	-	-
5	113.93 (C)	-	-
6	152.28 (C)	-	-
7	142.28 (C)	-	-

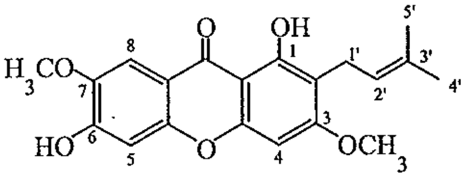
Table 12 (Continued)

Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
7-OCH_3	62.02 (OCH_3)	3.80 (*s*, 3H)	C-7
8	133.90 (C)	-	-
8a	111.96 (C)	-	-
9	182.38 (C=O)	-	-
9a	103.56 (C)	-	-
10a	153.52 (C)	-	-
1′	22.44 (CH_2)	3.46 (*br d*, 7.0 Hz, 2H)	C-2, C-3, C-2′, C-3′
2′	121.54 (CH)	5.31 (*br t*, 6.5 Hz, 1H)	C-1′, C-3′, C-4′
3′	135.67 (C)	-	-
4′	25.86 (CH_3)	1.78 (*d*, 1.0 Hz, 3H)	C-2′, C-3′, C-5′
5′	17.93 (CH_3)	1.85 (*d*, 0.5 Hz, 3H)	C-1′, C-2′, C-3′
1″	22.64 (CH_2)	3.57 (*br d*, 7.5 Hz, 2H)	C-5, C-6, C-10a, C-2″, C-3″
2″	121.14 (CH)	5.29 (*br t*, 6.5 Hz, 1H)	C-4″, C-5″
3″	132.67 (C)	-	-
4″	25.80 (CH_3)	1.69 (*d*, 1.0 Hz, 3H)	C-5, C-2″, C-3″, C-5″
5″	17.97 (CH_3)	1.88 (*d*, 0.5 Hz, 3H)	C-2″, C-3″, C-4″
1‴	26.57 (CH_2)	4.08 (*br d*, 6.0 Hz, 2H)	C-7, C-8, C-8a, C-2‴, C-3‴
2‴	123.59 (CH_3)	5.27 (*br t*, 6.5 Hz, 1H)	C-8, C-4‴, C-9‴
3‴	135.29 (C)	-	-

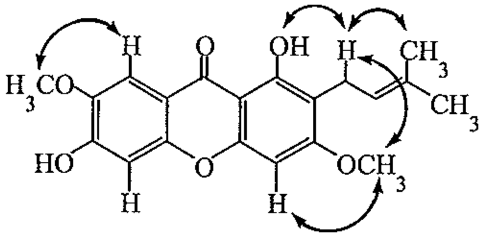
Table 12 (Continued)

Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
4'''	39.72 (CH_2)	1.90-2.02 (*m*, 2H)	C-2''', C-3''', C-9''', C-5'''
5'''	26.34 (CH_2)	2.03-2.08 (*m*, 2H)	C-4''', C-6''', C-7'''
6'''	124.32 (CH)	5.03 (*mt*, 7.0, 1.5 Hz, 1H)	C-8''', C-10''
7'''	131.26 (C)	-	-
8'''	25.62 (CH_3)	1.60 (*d*, 1.0 Hz, 3H)	C-4''', C-6''', C-7''', C-10'''
9'''	16.46 (CH_3)	1.83 (*d*, 1.0 Hz, 3H)	C-1''', C-2''', C-3'''
10'''	17.67 (CH_3)	1.55 (*d*, 0.5 Hz, 3H)	C-6''', C-7''', C-8'''

3.1.8 PGC8: 1,6-dihydroxy-3, 7-dimethoxy-2- (3-methyl-2-butenyl)xanthone

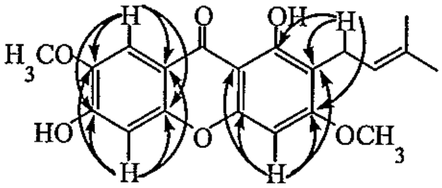


PGC8 was obtained as a pale-yellow solid, m.p. 252-253°. The UV spectrum showed maximum absorption bands at 360, 319, 300, 260 and 242 nm. The IR spectrum showed the absorption bands of hydroxy group at 3216 cm^{-1} and conjugated carbonyl group at 1655 cm^{-1}. The ^1H NMR spectrum (Table 13) showed a sharp singlet signal of hydroxy proton C1-OH at δ 13.00 and broad singlet signal of free hydroxy proton at δ 6.34. These signals were supported to be hydroxy proton by signal disappearance upon addition of D_2O. Two methoxy signals at δ 3.92 and δ 4.01 were assigned for C3-OCH_3 and C7-OCH_3. The appearance of three singlet signals of three isolated aromatic protons at δ 6.43, 6.94 and 7.61 were assigned for H-4, H-5 and H-8, respectively. The deshielded aromatic proton at δ 7.61 was assigned to be at C-8 due to an anisotropic effect of the carbonyl group. This was further supported by the differential NOE technique; irradiation of C3-OCH_3 effected the signal of H-4 (12%), and irradiation of C7-OCH_3 effected the signal of H-8 (8.5%). Thus the assignment of three aromatic protons and two methoxy groups were confirmed. The presence of an isoprenyl side chain were shown in the spectrum, of which the two singlet signals of *gem*-dimethyl protons (H-4′and H-5′) were at δ 1.68 and 1.80, a doublet signal of benzylic methylene protons (H-1′) was at δ 3.37 and a broad triplet signal of olefinic methine proton (H-2′) was at δ 5.24.



NOE of **PGC8**

The location of aromatic proton H-5 was indicated by the ^2J coupling of H-5 to C-6 and C-10a and the ^3J coupling of H-5 to C-7 and C-8a. Whereas the position of aromatic proton H-4 (δ6.43) was indicated by the ^2J coupling of H-4 to C-4a and C-3, the ^3J coupling of H-4 to C-2 and C-9a and the ^4J coupling of H-4 to C-9 on the HMBC experiment. The ^{13}C NMR spectral data (Table 13) deduced from DEPT and HMQC spectra showed 19 signals for 20 carbon atoms: a carbonyl carbon (δ 179.86), two methyl carbons (δ 25.80 and 17.80), a methylene carbon (δ 21.36), four methine carbons (δ 122.21, 104.62, 102.49 and 89.58), two methoxy carbons (δ 56.53 and 55.90) and ten quaternary carbons (δ 163.85, 159.36, 156.24, 152.54, 152.37, 144.32, 131.83, 113.63, 111.76 and 104.62).



Major HMBC of **PGC8**

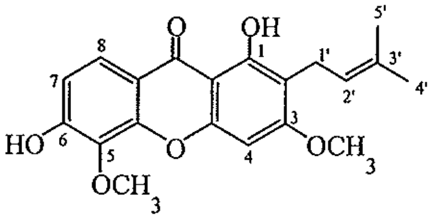
The isoprenyl unit was assigned to be at C-2 according to the correlations of H-1′ (δ3.37) to C-1, C-2 and C-3. The methoxy groups were assigned to be at C-3 and C-7 according to the ^3J coupling of methoxy protons at δ3.92 to C-3 and methoxy protons at δ4.01 to C-7 in HMBC experiment.

The assignment suggested that **PGC8** was 1,6-dihydroxy-3,7-dimethoxy-2-(3-methyl-2-butenyl)xanthone. This compound appears to be novel.

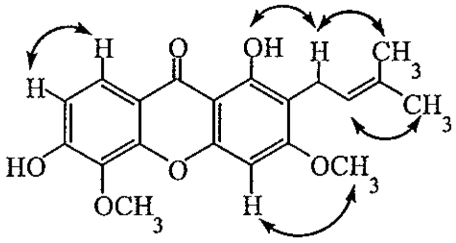
Table 13 The NMR spectral data of **PGC8**

Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.36 (C)	13.00 (*s*, OH)	C-2
2	111.76 (C)	-	-
3	163.85 (C)	-	-
4	89.58 (CH)	6.43 (*s*, 1H)	C-2, C-3, C-4a, C-9, C-9a
4a	156.24 (C)	-	-
5	102.49 (CH)	6.94 (*s*, 1H)	C-6, C-7, C-8a, C-10a
6	152.37 (C)	6.34 (*s*, OH)	-
7	144.32 (C)	-	-
8	104.62 (CH)	7.61 (*s*, 1H)	C-6, C-7, C-8a, C-9, C-10a
8a	113.63 (C)	-	-
9	179.86 (C=O)	-	-
9a	104.62 (C)	-	-
10a	152.54 (C)	-	-
3-OCH_3	55.90 (OCH_3)	3.92 (*s*, 3H)	C-3
7- OCH_3	56.53 (OCH_3)	4.01 (*s*, 3H)	C-7
1′	21.36 (CH_2)	3.37 (*br d*, 6.5 Hz, 2H)	C-1, C-2, C-3, C-2′, C-3′
2′	122.21 (CH)	5.24 (*br t*, 7.0 Hz, 1H)	
3′	131.83 (C)		
4′	25.80 (CH_3)	1.68 (*s*, 3H)	C-2′, C-3′, C-5′
5′	17.80 (CH_3)	1.80 (*s*, 3H)	C-2′, C-3′, C-4′

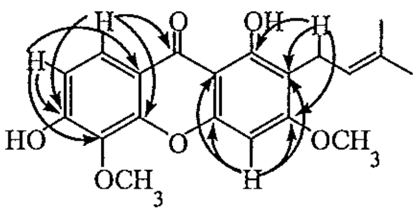
3.1.9 PGC9: 1,6-dihydroxy-3,5-dimethoxy-2-(3-methyl-2-butenyl)xanthone



PGC9 was obtained as a white-yellow solid, m.p. 152-153°. The UV spectrum showed maximum absorption bands at 345, 315, 281 and 246 nm. The IR spectrum showed absorption bands of the hydroxy group at 3375 cm^{-1} and the conjugated carbonyl group at 1652 cm^{-1}. The ^1H NMR spectrum (Table 14) exhibited the signals of hydroxy groups, two groups of two methoxy protons, an isolated aromatic proton, *ortho* aromatic protons and an isoprenyl side chain. The appearing of proton at δ 13.00 suggested that it was a hydroxy proton which formed intramolecular hydrogen bond to carbonyl group. The *ortho* coupled aromatic protons showed two doublet signals with J 9.0 Hz at δ 6.98 and δ 7.95. According to the lowfield chemical shift, these two protons were located at H-7 and H-8, nearby the carbonyl group. An isolated aromatic proton H-4 that resonated as a singlet at δ 6.48 was found on the NOE experiment to be *ortho* to a methoxy group which exhibited the signal at δ 3.95. Corresponding to HMBC experiment, the isolated aromatic proton was assigned for H-4 and then the methoxy group was at C-3. The remaining signal of methoxy protons appeared at δ 4.12 and it was placed at C-5. The spectrum further showed the typical signals of isoprenyl side chain, of which the signals of *gem*-dimethyl protons (H-4′and H-5′) appeared as two singlets at δ 1.68 and 1.80, the signal of benzylic methylene protons (H-1′) exhibited as a doublet at δ3.38 and olefinic methine proton (H-2′) showed as a broad triplet at δ5.23.



NOE of **PGC9**



Major HMBC of **PGC9**

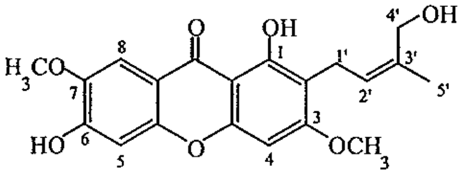
The arrangement of two methoxy groups at C3-OCH$_3$ and C5-OCH$_3$ were indicated by the ^3J coupling of methoxy protons to C-3 and C-5, respectively. The position of aromatic proton H-4 (δ6.48) was indicated by the ^2J coupling of H-4 to C-4a and C-3, the ^3J coupling of H-4 to C-2 and C-9a and the ^4J coupling of H-4 to C-9. This was further supported by the differential NOE technique; irradiation at the methoxy proton signal (δ 3.95) gave the enhancement of the signal of H-4 (11%). The position of deshielded aromatic proton H-8 was supported by the correlations of the H-8 to C-6, C-9 and C-10a. The doublet aromatic proton at δ6.98 was assigned to C-7 by the ^2J coupling of H-7 to C-6 and the ^3J coupling of H-7 to C-8a and C-5. The placement of the isoprenyl unit was assigned to be at C-2 and it was supported by the correlations of H-1′(δ3.38) to C-1, C-2 and C-3. The ^{13}C NMR spectral data (Table 14) deduced from DEPT and HMQC spectra showed 20 signals for 20 carbon atoms: a carbonyl carbon (δ 180.07), two methyl carbons (δ 25.78 and 17.78), a methylene carbon (δ21.59), four methine carbons (δ122.03, 122.00, 112.24 and 89.78), two methoxy carbons (δ61.95 and 55.97) and ten quaternary carbons (δ164.08, 159.78, 155.70, 154.11, 149.53, 133.59, 131.93, 115.26, 112.34 and 103.24).

The assignment then suggested that **PGC9** is 1,6-dihydroxy-3,5-dimethoxy-2-(3-methyl-2-butenyl)xanthone. This compound is an isomer of **PGC8** and appears to be novel.

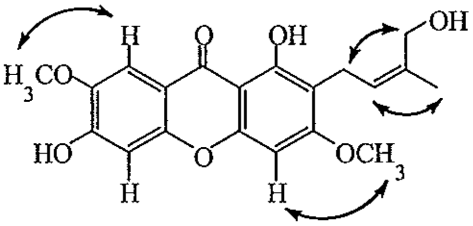
Table 14 The NMR spectral data of **PGC9**

Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.77 (C)	13.00 (*s*, OH)	C-1, C-2, C-9a
2	112.34 (C)	-	-
3	164.07 (C)	-	-
4	89.78 (CH)	6.48 (*s*, 1H)	C-2, C-3, C-4a, C-9, C-9a
4a	155.74 (C)	-	-
5	133.59 (C)	-	-
6	154.11 (CH)	6.29 (*s*, 1H)	C-5, C-6, C-7
7	112.24 (CH)	6.98 (*d*, 9.0 Hz, 1H)	C-5, C-6, C-8a
8	122.03 (CH)	7.95 (*d*, 9.0 Hz, 1H)	C-6, C-9, C-10a
8a	115.26 (C)	-	-
9	180.07 (C=O)	-	-
9a	103.24 (C)	-	-
10a	149.53 (C)	-	-
3-OCH_3	55.97 (OCH_3)	3.95 (*s*, 3H)	C-3
5- OCH_3	61.95 (OCH_3)	4.02 (*s*, 3H)	C-5
1′	21.59 (CH_2)	3.38 (*br d*, 7.0 Hz, 2H)	C-1, C-2, C-3, C-2′, C-3′
2′	122.00 (CH)	5.23 (*br t*, 7.0 Hz, 1H)	-
3′	131.93 (C)	-	-
4′	17.78 (CH_3)	1.80 (*s*, 3H)	C-2′, C-3′, C-5′
5′	25.78 CH_3)	1.68 (*s*, 3H)	C-2′, C-3′, C-4′

3.1.10 PGC10: 1,6-dihydroxy-3,7-dimethoxy-2-(4-hydroxy-3-methyl-2-butenyl) xanthone

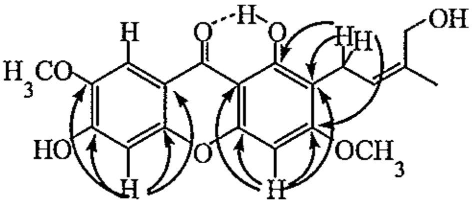


PGC10 was obtained as a white-yellow solid, m.p. 222-224°. The UV spectrum showed maximum absorption bands at 362, 316 and 235 nm. The IR spectrum showed absorption bands of the conjugated carbonyl group at 1654 cm^{-1} and the hydroxy group at 3408 cm^{-1}, indicating the xanthone nucleus. The ^1H NMR spectrum (Table 15) showed the singlet signal of a deshielded proton at δ13.37, two singlet resonances of two groups of methoxy protons at δ3.97 and 4.00, three singlet signals of three isolated aromatic protons at δ6.53, 6.93 and 7.58. These resonances and their chemical shifts were found to be in the same pattern as **PGC8**, therefore the placements of these protons were deduced as for **PGC8**, that was C1-OH (δ13.37), C3-OCH_3 (δ3.97), C7-OCH_3 (δ4.00), H-4 (δ6.53), H-5 (δ6.93) and H-8 (δ7.58). The enhancements of H-4 and H-8 which were caused by irradiation at C3-OCH_3 (δ3.97) and C7-OCH_3 (δ4.00), respectively, in the NOE experiment supported that C3-OCH_3 was adjacent to H-4 and C7-OCH_3 was next to H-7. The remaining resonances in the NMR spectrum which were a doublet signal of methyl protons (H-5′) at δ1.76, a doublet signal of benzylic methylene protons (H-1′) at δ3.42, a broad triplet signal of an olefinic methine proton (H-2′) at δ5.34 and a broad singlet resonance of the oxymethylene protons (H_2-4′) at δ4.32, implied a 4-hydroxy-3-methyl-2-butenyl side chain.



NOE of **PGC10**

The configuration of side chain was deduced from NOE experiments. Irradiation at hydroxymethylene protons (H-4′) at δ4.32 gave the enhancement to the signal of H-1′, whereas irradiation at the signal of olefinic methine proton H-2′ effected methyl protons (H-5′). This result suggested that the hydroxymethylene protons (H-4′) was *cis* to benzylic methylene protons (H-1′). The arrangement of the side chain was proposed to be at C-2 from the correlations of benzylic methylene protons H-1′ to C-1, C-2 and C-3. The ^{13}C NMR spectral data (Table 15) deduced from DEPT and HMQC spectra showed 20 signals for 20 carbon atoms: a carbonyl carbon (δ 180.14), a methyl carbons (δ 21.61), a methylene carbon (δ 21.13), four methine carbons (δ 124.85, 105.21, 103.17 and 90.19), two methoxy carbons (δ 56.49 and 56.30), an oxymethylene carbon (δ61.29) and ten quaternary carbons (δ164.06, 159.55, 156.68, 154.45, 152.98, 146.25, 135.54, 113.30, 111.00 and 103.17).



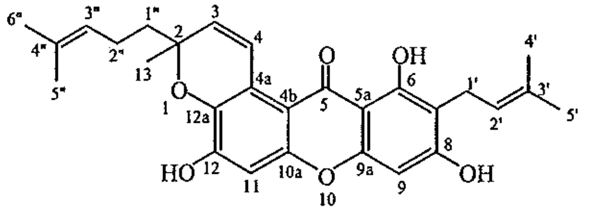
Major HMBC of **PGC10**

The structure of **PGC10** then was elucidated to be 1,6-dihydroxy-3,7-dimethoxy-2-(3-hydroxymethyl-2-butenyl)xanthone. It was a new natural occurring xanthone.

Table 15 The NMR spectral data of **PGC10**

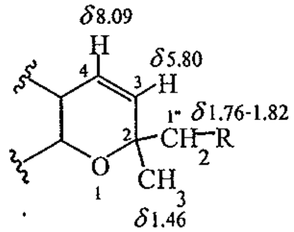
Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
1	159.55 (C)	13.37 (*s*, OH)	C-1, C-2, C-5
2	111.00 (C)	-	-
3	164.06 (C)	-	-
4	90.19 (CH)	6.53 (*s*, 1H)	C-2, C-3, C-4a, C-5
4a	156.68 (C)	-	-
5	103.17 (CH)	6.93 (*s*, 1H)	C-6, C-7, C-8a, C-10a
6	152.98 (C)	-	-
7	146.25 (C)	-	-
8	105.21 (CH)	7.58 (*s*, 1H)	C-6, C-7, C-9, C-10a
8a	113.30 (C)	-	-
9	180.14 (C=O)	-	-
9a	103.17 (C)	-	-
10a	154.45 (C)	-	-
3-OCH_3	56.30 (OCH_3)	3.97 (*s*, 3H)	C-3
7-OCH_3	56.48 (OCH_3)	4.00 (*s*, 3H)	C-7
1′	21.13 (CH_2)	3.42 (*br d*, 8.0 Hz, 2H)	C-1, C-2, C-3, C-2′, C3′
2′	124.85 (CH)	5.34 (*br t*, 7.5 Hz, 1H)	-
3′	135.54 (C)	-	-
4′	61.29 (CH_2O)	4.32 (*s*, 2H)	C-2′, C-3′, C-5′
5′	21.61 (CH_3)	1.76(*d*, 1.0 Hz, 3H)	C-2′, C-3′, C-4′

3.1.11 PGC11: 6,8,12-trihydroxy-7-(3-methyl-2-butenyl)-2-methyl-2-(4-methyl-3-pentenyl)pyrano(2′,3′:7,8)xanthone



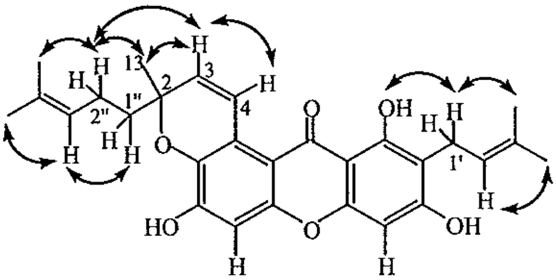
PGC11 is a yellow solid, m.p. 92-94°. The UV spectrum showed maximum absorption bands at 383, 323, 265 and 246 nm. The IR spectrum showed the absorption bands of hydroxy group at 3473 cm^{-1} and conjugated carbonyl group at 1652 cm^{-1}. The ^{1}H NMR spectrum (Table 16) exhibited a singlet signal of a chelated hydroxy group C6-OH at δ 13.74 and two sharp singlet signals of two free hydroxy groups at δ 6.22 and 6.18. These three signals were supported to be hydroxy proton by signal disappearance upon addition of D_2O. The spectrum also showed two sharp singlet signals of two isolated aromatic protons which were proposed to be H-9 and H-11 at δ 6.32 and 6.83, respectively. The appearing of the signals of two methyl groups at δ 1.78 (H-5′) and 1.85 (H-4′), methylene protons (H-1′) at δ 3.46 and an olefinic methine proton (H-2′) at δ 5.30 were suggestive to the signal of an isoprenyl moiety. Irradiation of the methylene protons (H_2-1′) at δ 3.46 caused an NOE enhancement of the chelated hydroxy proton C1-OH, these results suggested that the isoprenyl unit was at C-2. Two vicinal protons appearing as two doublets at δ 8.09 (H-4) and 5.80 (H-3) implied the presence of a chromene ring. The deshielded effect on resonance at δ 8.09 suggested that the chromene ring attached to the xanthone nucleus nearby carbonyl group. More informations of the chromene ring were obtained from the NOE experiment that was irradiation of olefinic proton (H-3) δ 5.80 caused an enhancement

of the multiplet signal of methylene protons (H-1″) at δ 1.80 and a singlet signal of methyl protons (H-13) at δ 1.46. This evidence indicated that the chromene ring consisted of a methyl group and CH_2-R as shown in the structural unit A.



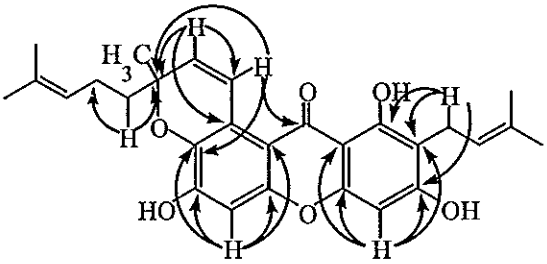
structural unit A

The remaining resonances in the spectrum were proposed to be the resonances of the R group. Those resonances were displayed as follow: two singlets of two methyl groups at δ 1.56 (H-6″) and 1.67 (H-5″), a broad triplet of an olefinic proton (H-3″) at δ 5.10 and a multiplet of methylene protons (H-2″) at δ 2.09-2.17. Accordingly, isoprenyl unit was suggested to be R group of structure unit A. On decoupling experiment, it was found that irradiation at olefinic proton H-3″ (δ 5.10) caused the collapsion of the signal of methylene protons H-2″ (δ 2.09-2.17). Furthermore irradiation at the methylene protons H-2″ (δ 2.09-2.17) effected the signal of the methylene protons H-1″ (δ 1.76-1.82). These results indicated that R group was an isoprenyl unit. The arrangement of the aromatic protons and substituent unit was confirmed by HMBC. The placement of aromatic protons H-9 and H-11 were supported by the cross peaks of H-9 to C-5a, C-7, C-8 and C-9a and H-11 to C-4b, C-10a, C-12 and C-12a.



NOE of **PGC11**

The correlations of benzylic methylene protons (H-1′) δ 3.46 to C-6, C-7 and C-8 supported the position of isoprenyl side chain at C-7. The location of methyl group on chromene ring was supported by the correlations of methyl protons (H-13) at δ 1.46 to C-1″, C-2 and C-3. The connection of C-6 side chain to chromene ring at C-2 was supported by the ^2J coupling of methylene protons (H-1″) at δ 1.76-1.82 to C-2. The ^{13}C NMR spectral data (Table 16) deduced from DEPT and HMQC spectra showed 28 signals for 28 carbon atoms: a carbonyl carbon (δ 182.55), five methyl carbons (δ 25.86, 25.67, 25.65, 17.93 and 17.67), three methylene carbons (δ 40.38, 22.77 and 21.45), six methine carbons (δ 131.45, 123.65, 121.44, 121.39, 102.32 and 93.42) and thirteen quaternary carbons (δ 161.73, 160.47, 155.34, 153.03, 150.77, 136.82, 135.86, 132.16, 119.58, 108.55, 108.36, 103.78 and 79.39).



Major HMBC of **PGC11**

PGC11 was then identified as 6,8,12-trihydroxy-7-(3-methyl-2-butenyl)-2-methyl-2-(4-methyl-3-pentenyl)pyrano(2′,3′:7,8)xanthone. This compound was a new xanthone derivative.

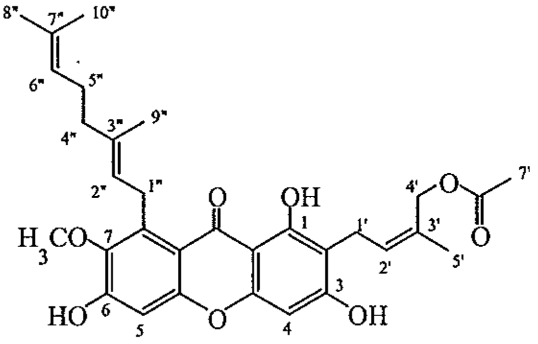
Table 16 The NMR spectral data of **PGC11**

Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
2	79.39 (C)	-	-
3	131.45 (CH)	5.80 (*d*, 10.0 Hz, 1H)	C-2, C-4, C-4a
4	121.44 (CH)	8.09 (*d*, 10.0 Hz, 1H)	C-2, C-4b, C-12a
4a	119.58 (C)	-	-
4b	108.55 (C)	-	-
5	182.55 (C=O)	-	-
5a	103.78 (C)	-	-
6	160.47 (C)	13.74 (*s*, OH)	C-6, C-7, C-5a
7	108.36 (C)	-	-
8	161.73 (C)	-	-
9	93.42 (CH)	6.32 (*s*, 1H)	C-5, C-5a, C-7, C-8, C-9a
9a	155.34 (C)	-	-
10a	153.03 (C)	-	-
11	102.32 (CH)	6.83 (*s*, 1H)	C-4b, C-5, C-10a, C-12, C-12a
12	150.77 (C)	6.22 (*br s*, OH)	C-10a, C-11, C-12, C-12a
12a	136.82 (C)	-	-
13	25.65 (CH_3)	1.46 (*s*, 3H)	C-2, C-3, C-1″

Table 16 (Continued)

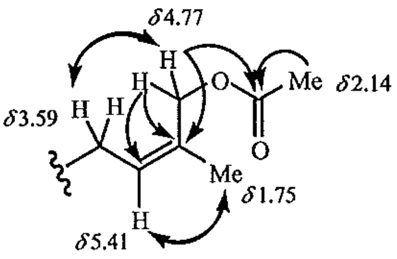
Position	δ_c (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
1′	21.45 (CH_2)	3.46 (*br d*, 7.0 Hz, 2H)	C-6, C-7, C-8, C-2′, C-3′
2′	121.39 (CH)	5.30 (*br t*, 7.0 Hz, 1H)	C-1′, C-4′, C-5′
3′	135.86 (C)	-	-
4′	17.93 (CH_3)	1.85 (*d*, 0.5 Hz, 3H)	C-2′, C-3′, C-5′
5′	25.86 (CH_3)	1.78 (*d*, 1.0 Hz ,3H)	C-2′, C-3′, C-4′
1″	40.38 (CH_2)	1.76-1.82 (*m*, 2H)	C-2, C-2″
2″	22.77 (CH_2)	2.09-2.17 (*m*, 2H)	C-3″, C-4″
3″	123.65 (CH)	5.10 (*br t*, 7.0 Hz, 1H)	C-2″, C-5″, C-6″
4″	132.16 (C)	-	-
5″	25.67 (CH_3)	1.67 (*s*, 3H)	C-3″, C-4″, C-6″
6″	17.67 (CH_3)	1.58 (*s*, 3H)	C-3″, C-4″, C-5″

3.1.12 PGC12: 1,3,6-trihydroxy-7-methoxy-2-(3-methyl-4-*O*-acetyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl) xanthone



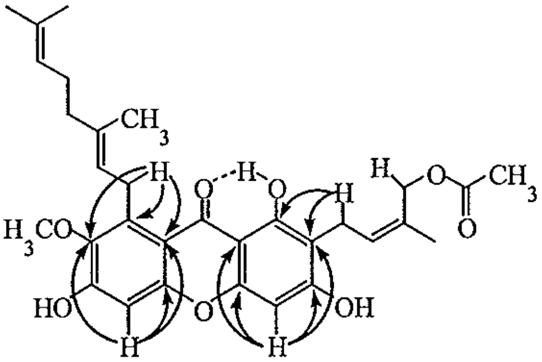
PGC12 is a yellow viscous liquid. The UV spectrum showed maximam absorption bands at 362, 312, 262 and 244 nm. IR spectrum showed the absorption bands of carbonyl groups at 1711, 1641 cm^{-1} and hydroxy group at 3385 cm^{-1}. The ^{1}H NMR spectrum showed a singlet signal of deshielded proton C1-OH at δ 13.82, a singlet resonance of methoxy protons at δ3.81, two singlet signals of two isolated aromatic protons H-4 and H-5 at δ6.35 and 6.84. Two side chains were detected in the ^{1}H NMR data, one was a geranyl side chain and another was an isoprenyl unit with an ester group. The geranyl signals appeared as follow; two olefinic protons at δ 5.27 (H-2″) and 5.03 (H-6″), three sets of methylene groups at δ4.11 (H-1″), 2.03-2.08 (H-5″) and 1.90-2.02 (H-4″) and three vinylic methyl groups at δ 1.83 (H-9″), 1.60 (H-8″) and 1.55 (H-10″). The proton signals of isoprenyl with an ester group appeared as the same pattern of isoprenyl unit with hydroxy group of **PGC3**. Therefore, the proton signals of C_5 unit of **PGC12** were assigned as follow; a doublet of triplet at δ5.41, a doublet at δ3.59, a sharp singlet of two protons at δ4.77, a sharp singlet of three protons at δ 2.14 and a doublet at δ 1.75 which were the signals of olefinic

proton (H-2′), benzylic methylene protons (H-1′), oxymethylene protons (H-4′), methyl ester group (H-7′) and vinylic methyl protons (H-5′), respectively. This side chain was then identified to be the 3-methyl-4-*O*-acetyl-2-butenyl as shown in structural unit A.



NOE of structural unit A

This structural unit was confirmed by NOE and HMBC experiments. Irradiation of oxymethylene protons H-4′ (δ4.77) gave enhancement to benzylic methylene protons H-1′ (δ3.59). Irradiation of olefinic proton H-2′ (δ5.41) gave enhancement to vinylic methyl proton H-5′ (δ 1.75). The position of acetyl group was confirmed by correlations of acetyl protons H-7′ (δ2.14) and oxymethylene protons H-4′ (δ4.77) to carbonyl ester C-6′ (δ172.17) on HMBC spectrum. Since the chemical shifts and the NMR pattern of this compound were quite similar to that of **PGC3**, therefore the structure of **PGC12** was deduced as acetyl derivative of **PGC3**. The HMBC spectrum was used to support the structural assignment. The correlation of benzylic methylene protons H-1′ (δ3.59) to C-1 and C-2 confirmed the position of 3-methyl-4-*O*-acetyl-2-butenyl side chain to be at C-2. The geranyl side chain which was located at C-8 was confirmed by the correlations of benzylic methylene protons H-1″ (δ4.11) to C-7, C-8 and C-8a. The deduction of two aromatic protons H-4 and H-5 were supported by the correlations of H-4 to C-2, C-3, C-4a and C-9a and H-5 to C-7, C-8a and C-10a. The ^{13}C NMR spectral data (Table 17) deduced from DEPT and HMQC spectra showed 31 signals for 31 carbon atoms: two carbonyl carbons (δ 181.99 and 172.17), a methoxy carbon (δ 62.06), five methyl carbons (δ 25.61, 21.16, 20.99, 17.67 and 16.50), five methylene carbons (δ 63.92, 39.72, 26.59, 26.53 and 20.90), five methine carbons (δ 128.63, 124.33, 123.30, 101.60and 93.57) and thirteen quaternary carbon (δ 161.58, 160.86, 155.86, 155.30, 154.55, 142.64, 137.15, 135.57, 131.28, 130.45, 112.27, 108.03 and 103.48).



Major HMBC of **PGC12**

Thus the structure of **PGC12** was proposed to be 1,3,6-trihydroxy-7-methoxy-2-(3-methyl-4-*O*-acetyl-2-butenyl)-8-(3,7-dimethyl-2,6-octadienyl)xanthone. It was a new natural occurring xanthone.

Table 17 The NMR spectral data of **PGC12**

Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
1	160.86 (C)	13.83 (*s*, OH)	C-1, C-2, C-9a
2	108.03 (C)	-	-
3	161.58 (C)	-	-
4	93.57 (CH)	6.35 (*s*, 1H)	C-2, C-3, C-4a, C-9, C-9a

Table 17 (Continued)

Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
4a	155.30 (C)	-	-
6	154.55 (C)	-	-
7	142.64 (C)	-	-
8	137.15 (C)	-	-
8a	112.27 (C)	-	-
9	181.99 (C=O)	-	-
9a	103.48 (C)	-	-
10a	155.86 (C)	-	-
1′	20.90 (CH_2)	3.59 (*dd*, 7.0, 1.0 Hz, 2H)	C-1, C-2, C-2′, C-3′
2′	128.63 (CH)	5.41 (*dt*-like, 6.0 Hz, 1H)	C-2, C-5′, C-4′
3′	131.28 (C)	-	-
4′	63.92 (OCH_2)	4.77 (*s*, 2H)	C-2′, C-3′, C-5′, C-6′
5′	21.16 (CH_3)	1.75 (*d*, 1.0 Hz, 3H)	C-2′, C-3′, C-4′
6′	172.17 (C=O)	-	-
7′	20.99 (CH_3)	2.14 (*s*, 3H)	C-6′
7-OCH_3	62.06 (OCH_3)	3.81 (*s*, 3H)	C-7
1″	26.59 (CH_2)	4.11 (*br d*, 5.5 Hz, 2H)	C-7, C-8, C-8a, C-2″
2″	123.30 (CH)	5.27 (*br t*, 6.5 Hz, 1H)	C-8, C-1″, C-4″, C-9″
3″	135.57 (C)		
4″	39.72 (CH_2)	1.90-2.02 (*m*, 2H)	C-1″, C-2″, C-3″
5″	26.53 (CH_2)	2.03-2.08 (*m*, 2H)	C-4″
6″	124.33 (CH)	5.03 (*br t*, 7.0 Hz, 1H)	C-5″

Table 17 (Continued)

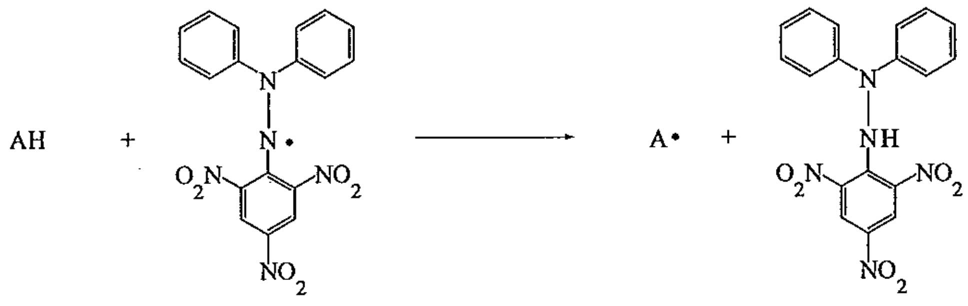
Position	δ_C (C-Type)	δ_H (*multiplicity*, J_{Hz})	HMBC
7″	130.45 (C)		
8″	25.61 (CH_3)	1.60 (*s*, 3H)	C-6″, C-7″, C-10″
9″	16.50 (CH_3)	1.83 (*d*, 0.5 Hz, 3H)	C-2″, C-3″, C-4″
10″	17.67 (CH_3)	1.55 (*s*, 3H)	C-5″, C-6″, C-7″, C-8″

3.2 Evaluation of Antioxidation Activity

Recently, natural antioxidants have attracted attention because some synthetic antioxidants have been found to be carcinogenic and harmful to lungs and liver. Phenolic compounds were known to be the antioxidant with an excellent hydrogen or electron donor (Shahidi, *et al.*, 1992). Most of components isolated from *G. cowa* were xanthones that contained free phenolic hydroxy group. It was thus of considerable interest in the studies of antioxidant activity.

Estimation of antioxidative effects has been carried out by various methods. The DPPH (α,α-diphenyl-β-picrylhydrazyl) method is one of the methods used for testing of antioxidative activity. DPPH is a stable free radical which shows a purple color and a strong absorption at 517 nm. It has been used as a convenient tool for the antioxidant assay of biological materials. When DPPH radical accepts hydrogen radical, a more stable compound will be form and consequently its characteristic absorption at 517 nm vanishes. The capacity of the substances to donate electrons can be estimated from the degree of loss of color (Blois, 1958).

Coexistence of an antioxidant compound (AH) and free radical DPPH leads to the disappearance of DPPH free radical and to the appearance the free radical A°



purple

3.2.1 Screening on the free radical scavenging activity of the crude material

To determine the scavenging activity, the latex of *G. cowa* was conducted at the final concentration at 50 μg/ml. The activity was monitored by following the decrease of the absorbance of the solution at 517 nm.

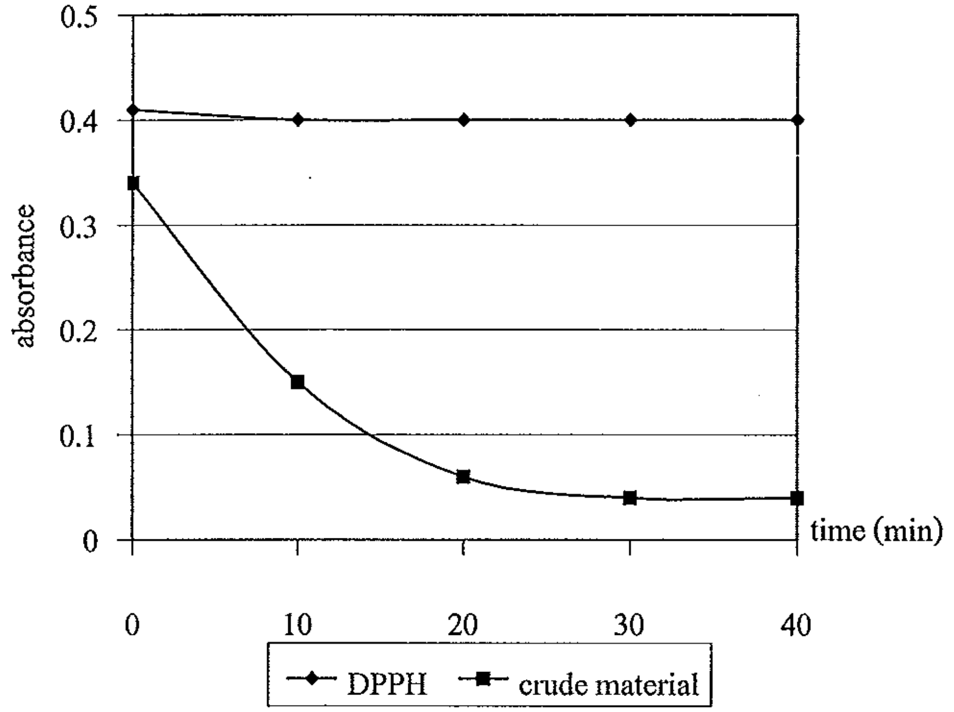


Figure 2 Antioxidation activity of the crude material against DPPH radical

The results (Figure 2) indicated that the crude material was able to scavenge the DPPH radical significantly.

The assessment of the antioxidation activity of the crude material was extended. In comparable to the standard antioxidant, BHT and the crude material were evaluated for IC_{50}. Since the decolorization occurred properly with in 30 min, the IC_{50} then was examined at 30 min.

Table 18 Inhibitory concentration (IC_{50}) of the crude material comparable to BHT

sample	IC_{50} (μg/ml, 30 min)
crude material	13.20
BHT	5.10

The results showed that the crude material showed IC_{50} at 13.20 μg/ml whereas BHT exhibited IC_{50} at 5.10 μg/ml.

3.2.2 Free radical scavenging activity of the pure compounds

To determine the active constituent of the latex of *G. cowa*, pure constituents were examined for the activity. The final concentration of the tested samples were conducted at final concentration 200 and 100 μM. The absorption of the solution of the tested samples and DPPH were measured at 517 nm after warm at 37° for 30 min. The activity was expressed in the percentage inhibition.

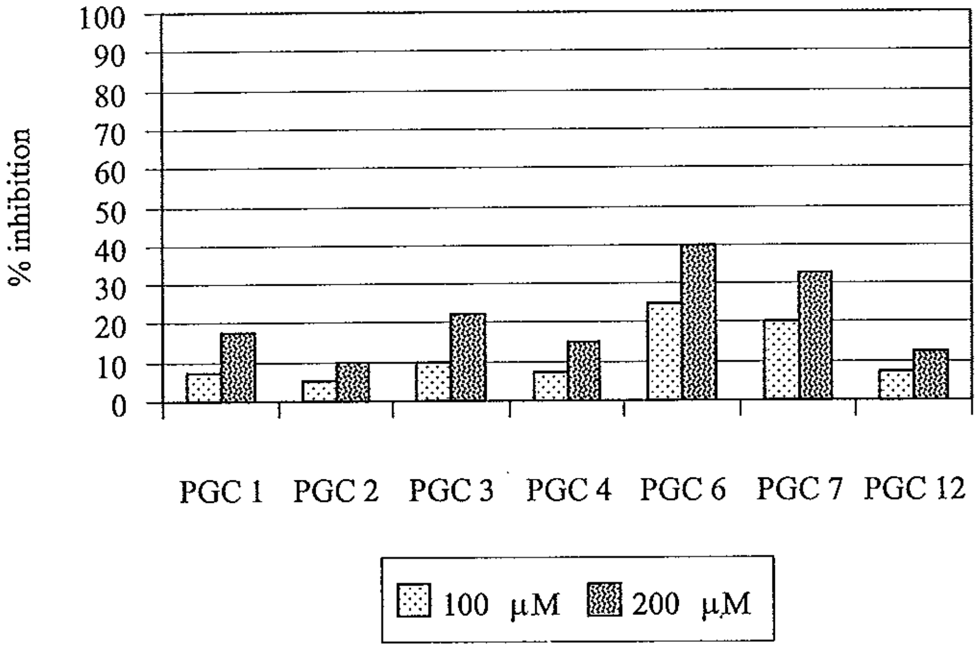


Figure 3 Radical scavenging activity of tested samples at 200 and 100 μM

Radical scavenging activities of some pure compounds from the latex of *G. cowa* were evaluated against the DPPH radical. **PGC1, 2, 3, 4, 6, 7** and **12** were found to scavenge the DPPH radical at the concentration over 100 μM. The results suggested that the radical scavenging activity of the crude material did not exhibit by **PGC1, 2, 3, 4, 6, 7** and **12.** Further search for the active fraction will be conducted.

APPENDIX

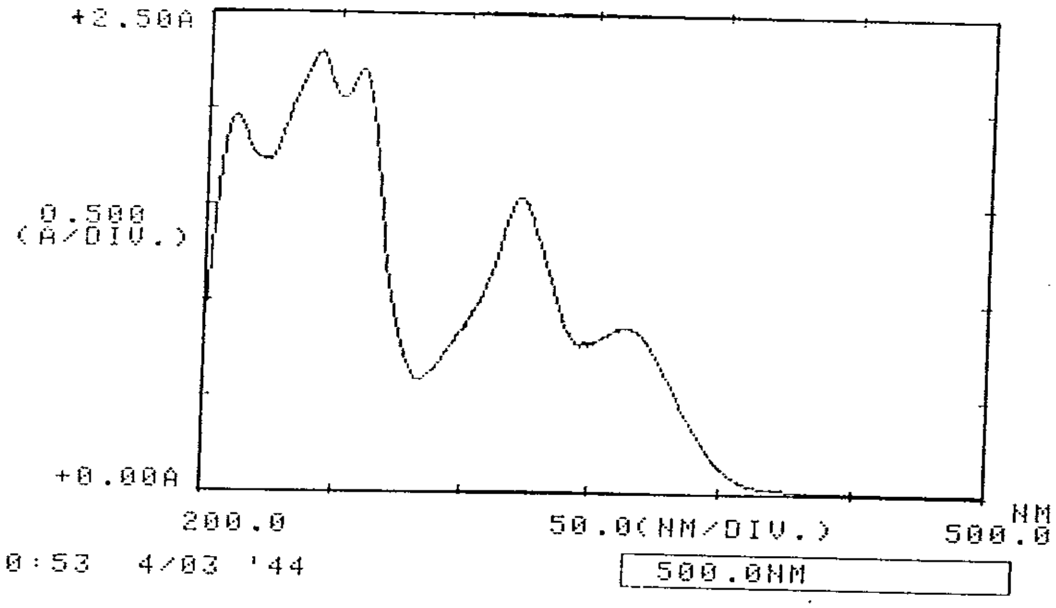


Figure 4 UV (EtOH) spectrum of **PGC1**

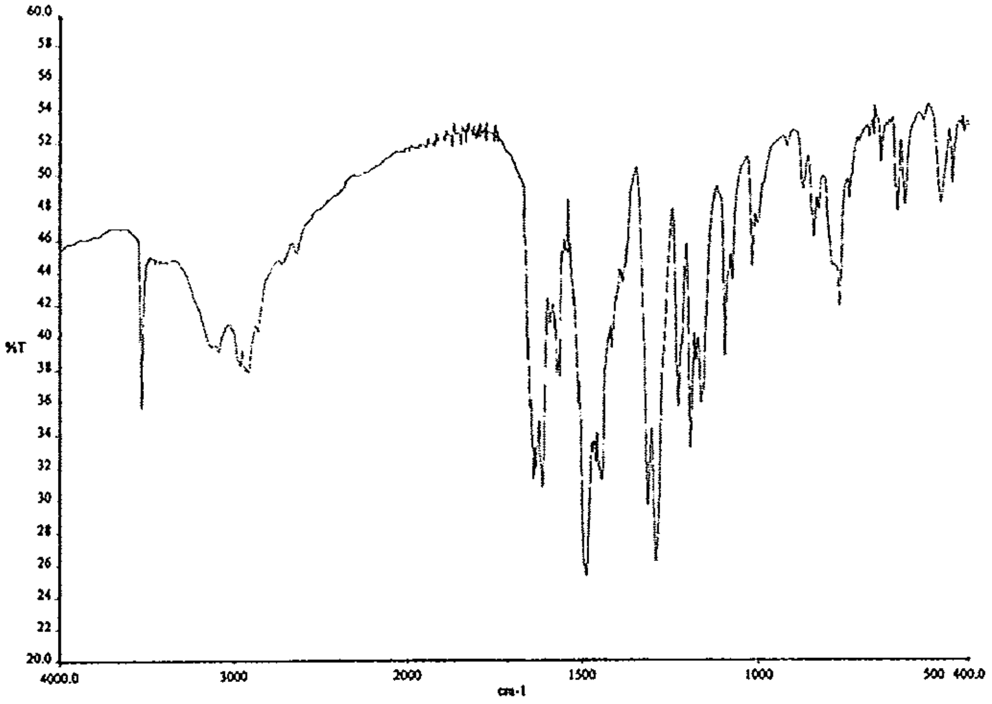


Figure 5 FT-IR (KBr) spectrum of **PGC1**

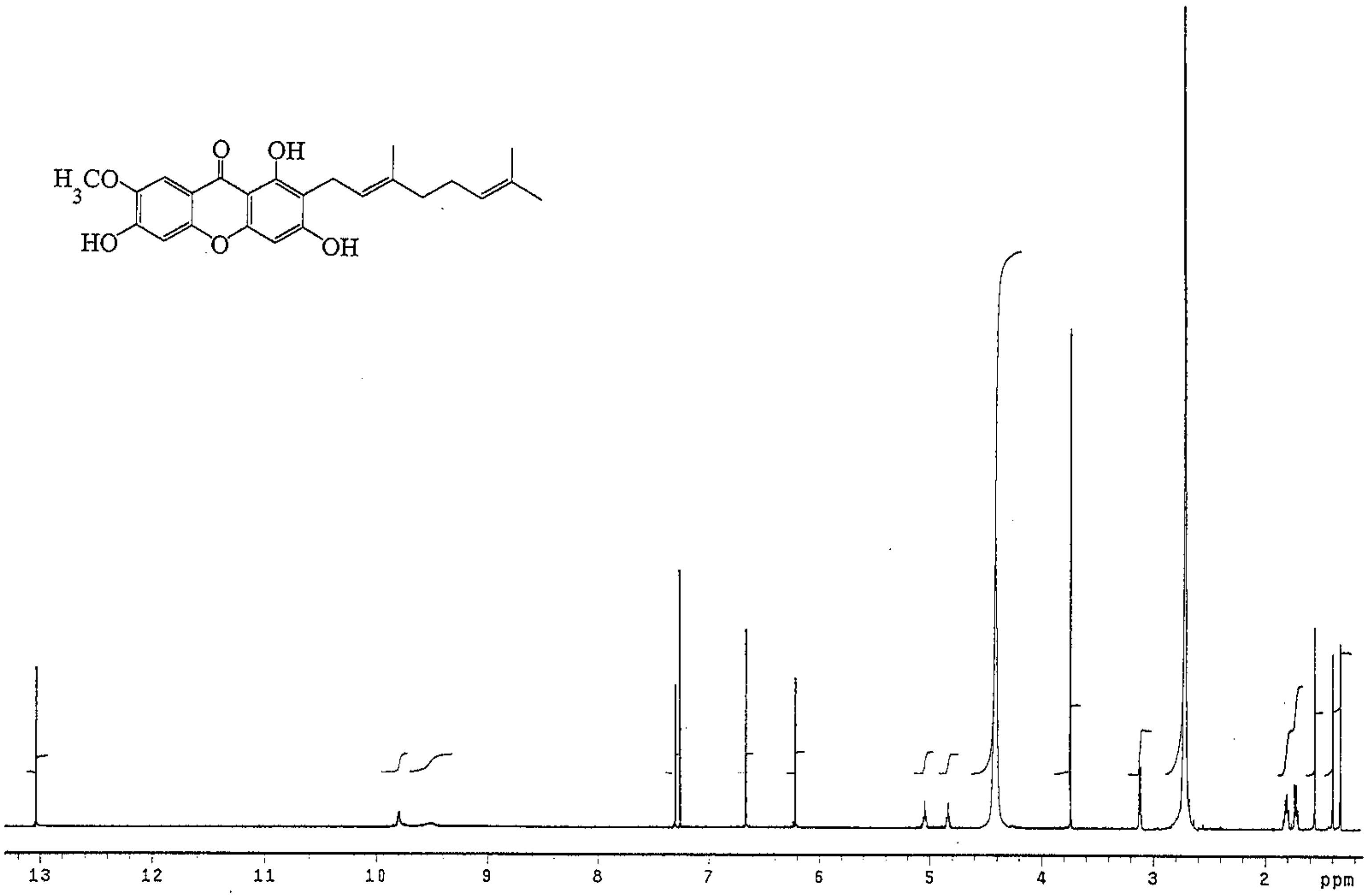


Figure 6 ^{1}H NMR (500 MHz)($CDCl_3$+DMSO-d_6) spectrum of **PGC1** (cowaxanthone)

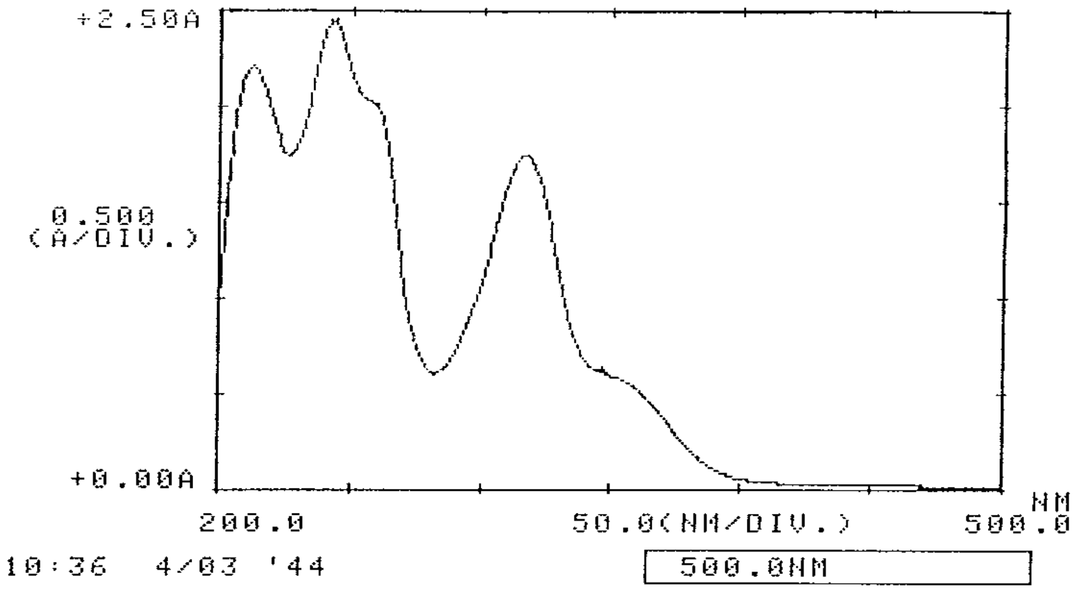


Figure 7 UV (EtOH) spectrum of **PGC2**

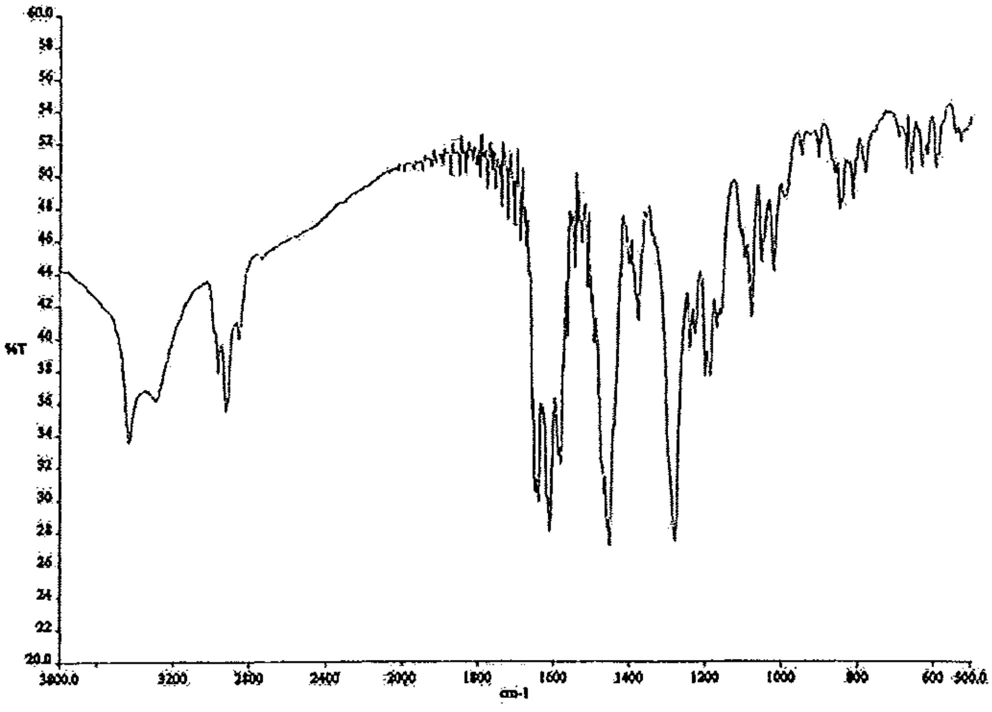


Figure 8 FT-IR (KBr) spectrum of **PGC2**

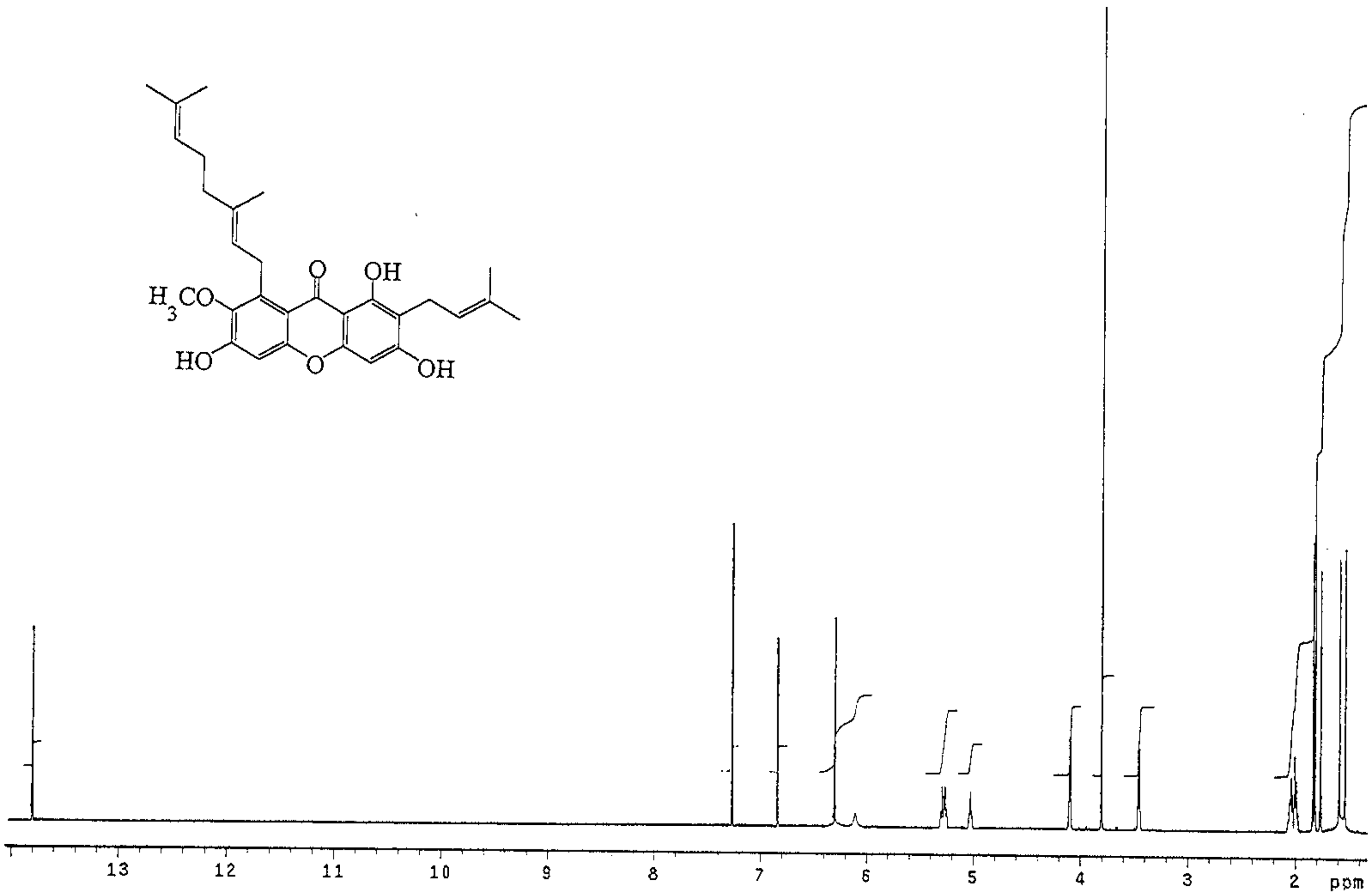


Figure 9 ^{1}H NMR (500 MHz)(CDCl$_3$) spectrum of **PGC2** (cowanin)

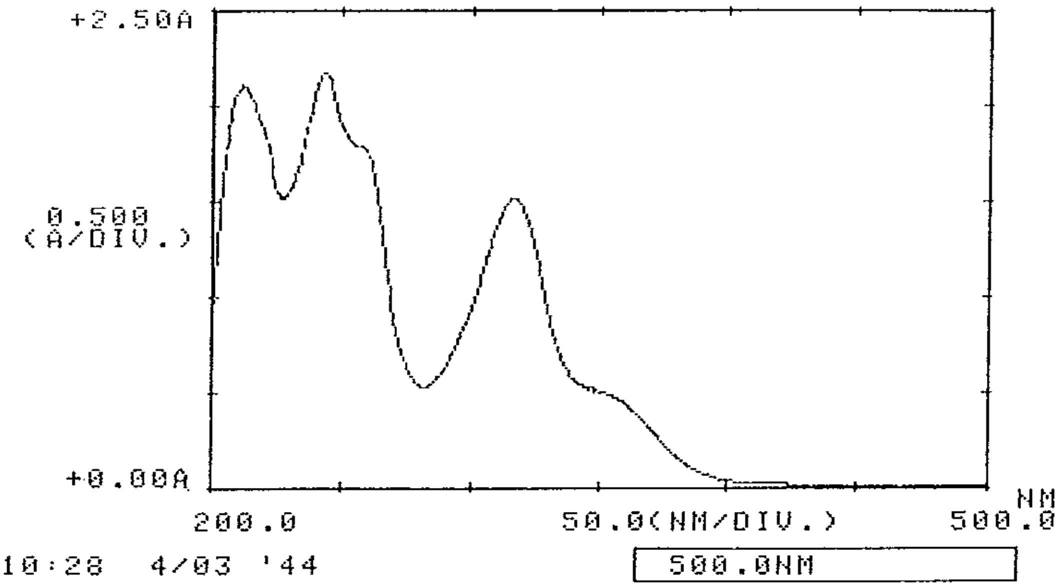


Figure 10 UV (EtOH) spectrum of **PGC3**

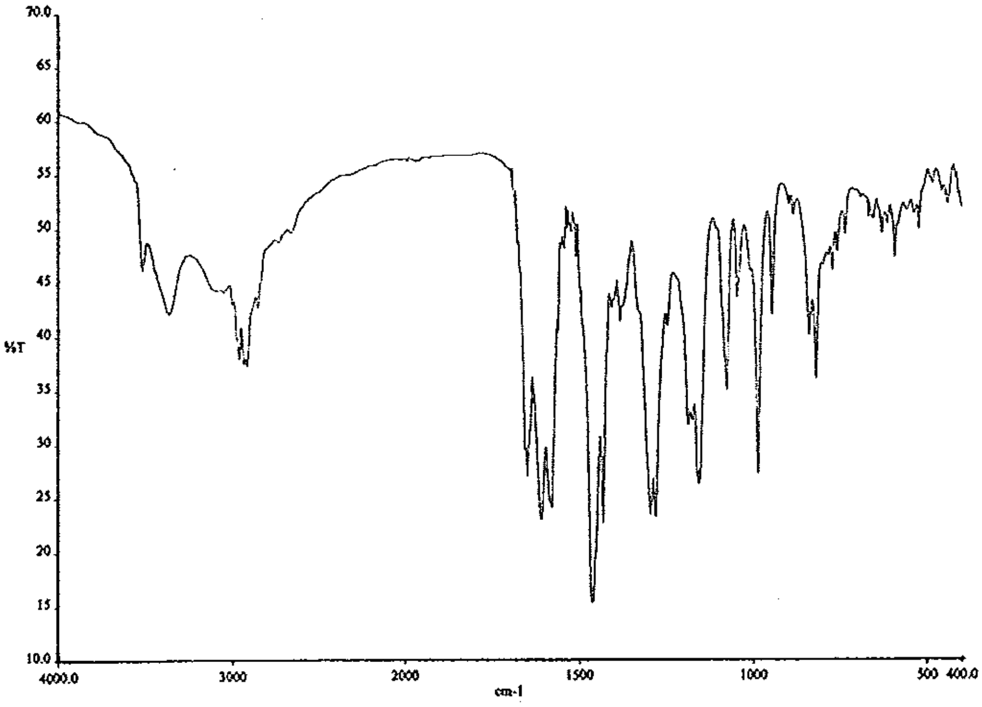


Figure 11 FT-IR (KBr) spectrum of **PGC3**

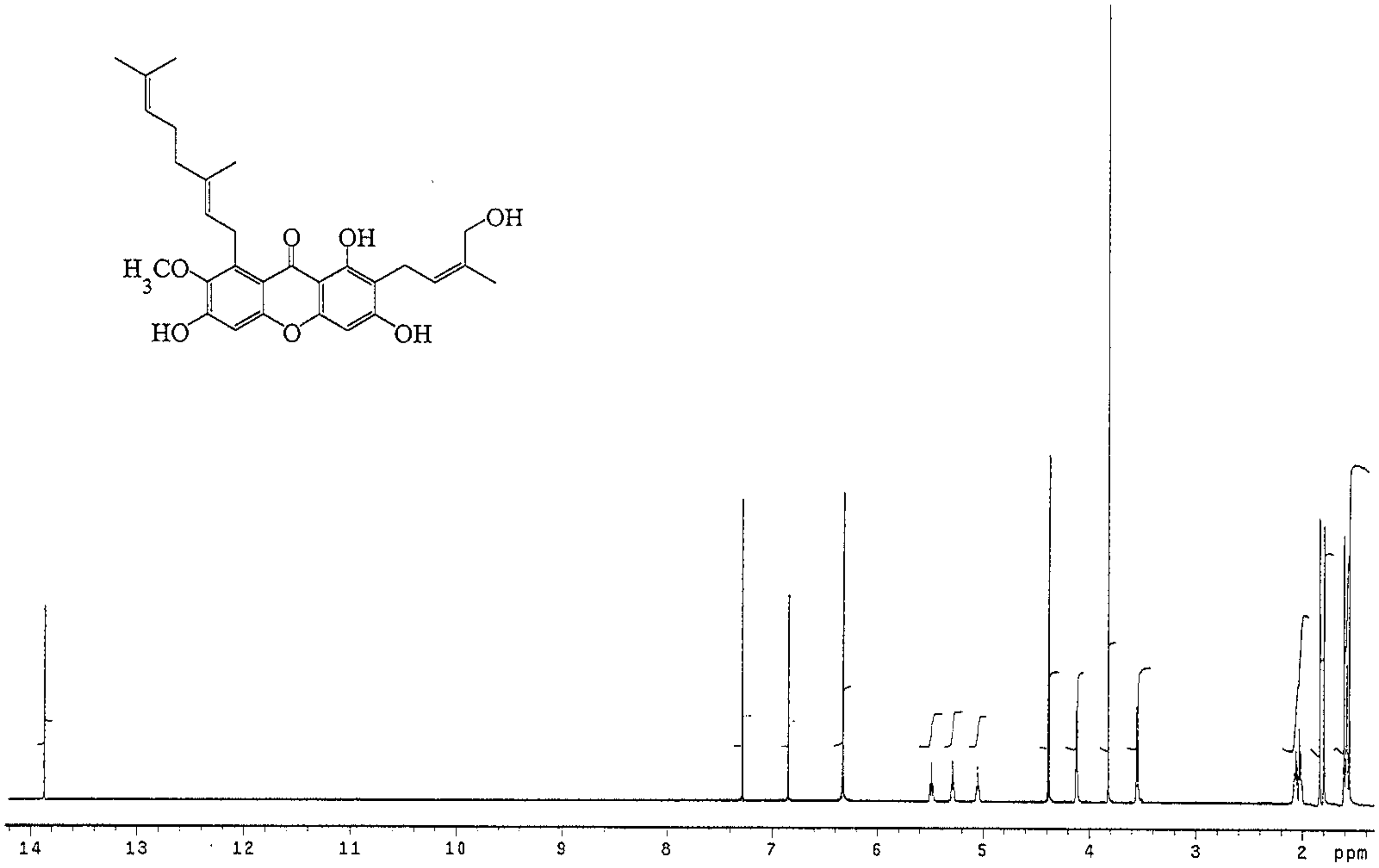


Figure 12 ^{1}H NMR (500 MHz)(CDCl$_3$) spectrum of **PGC3** (cowanol)

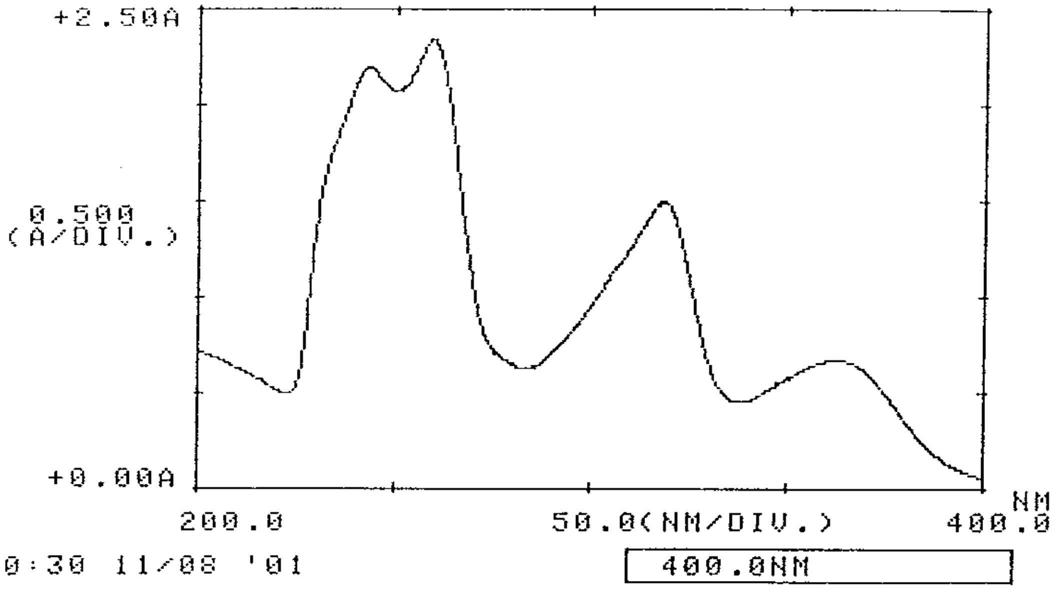


Figure 13 UV (EtOH) spectrum of **PGC4**

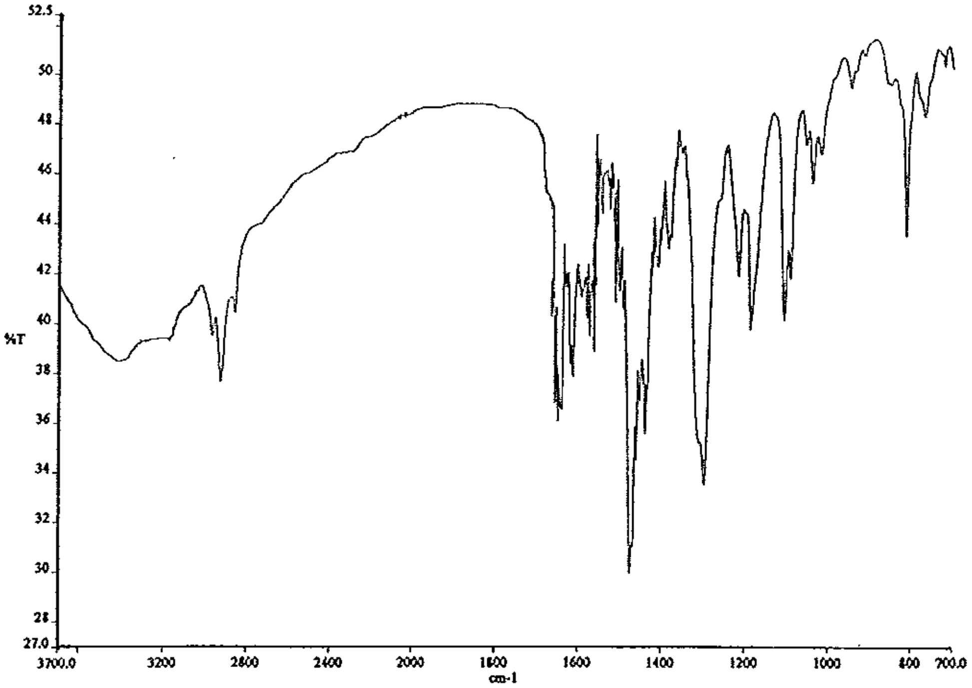


Figure 14 FT-IR (KBr) spectrum of **PGC4**

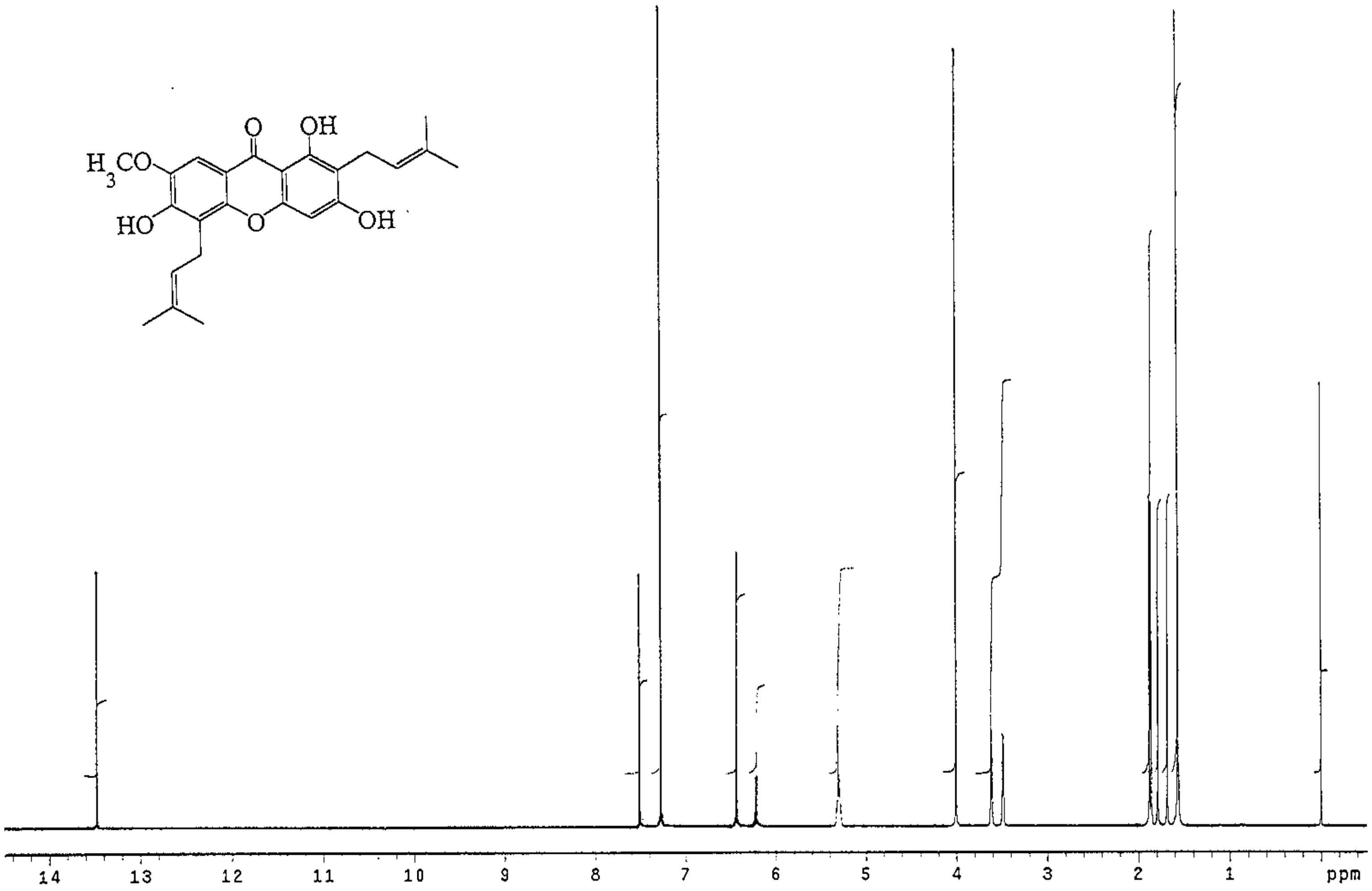


Figure 15 ^{1}H NMR (500 MHz)(CDCl$_3$) spectrum of **PGC4**

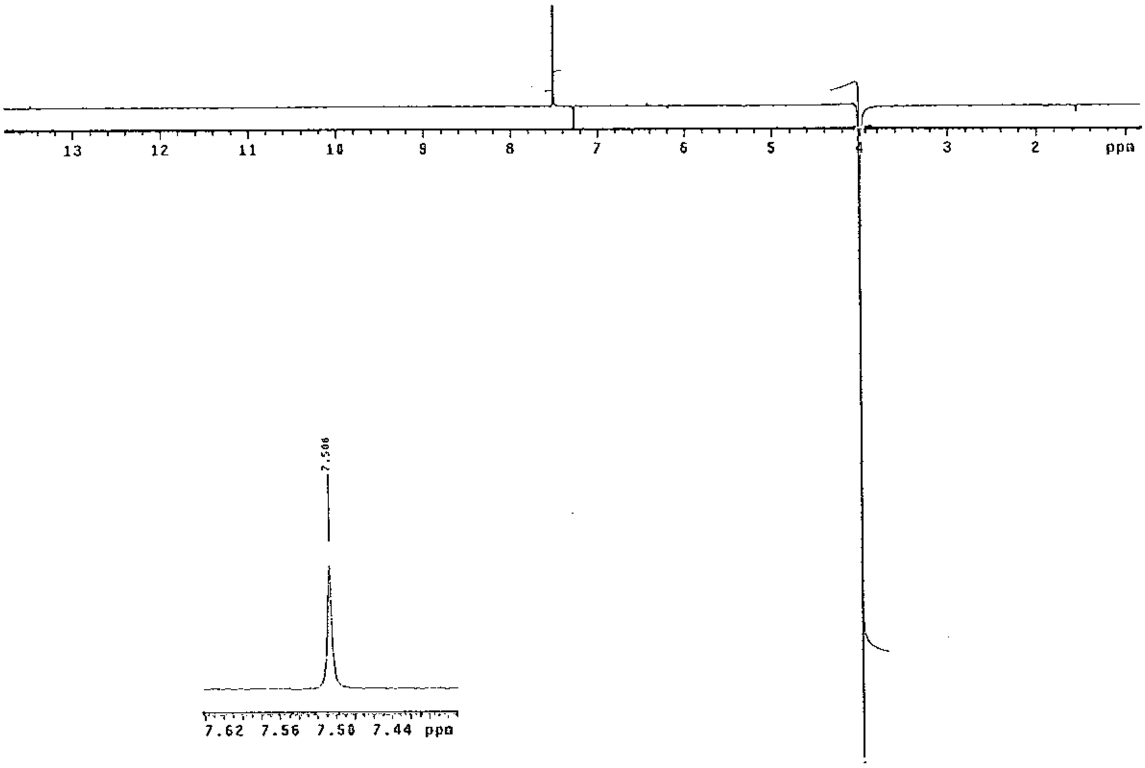


Figure 16 NOEDIFF spectrum of **PGC4** after irradiation at δ_H 4.00

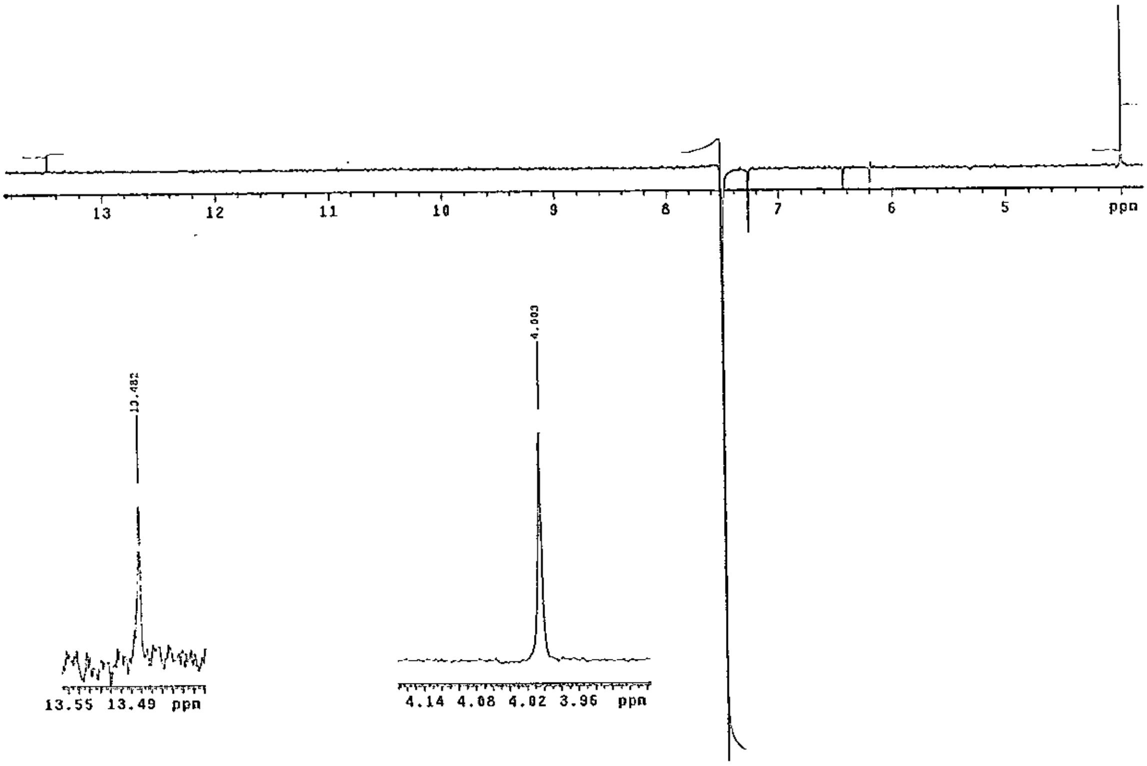


Figure 17 NOEDIFF spectrum of **PGC4** after irradiation at δ_H 7.51

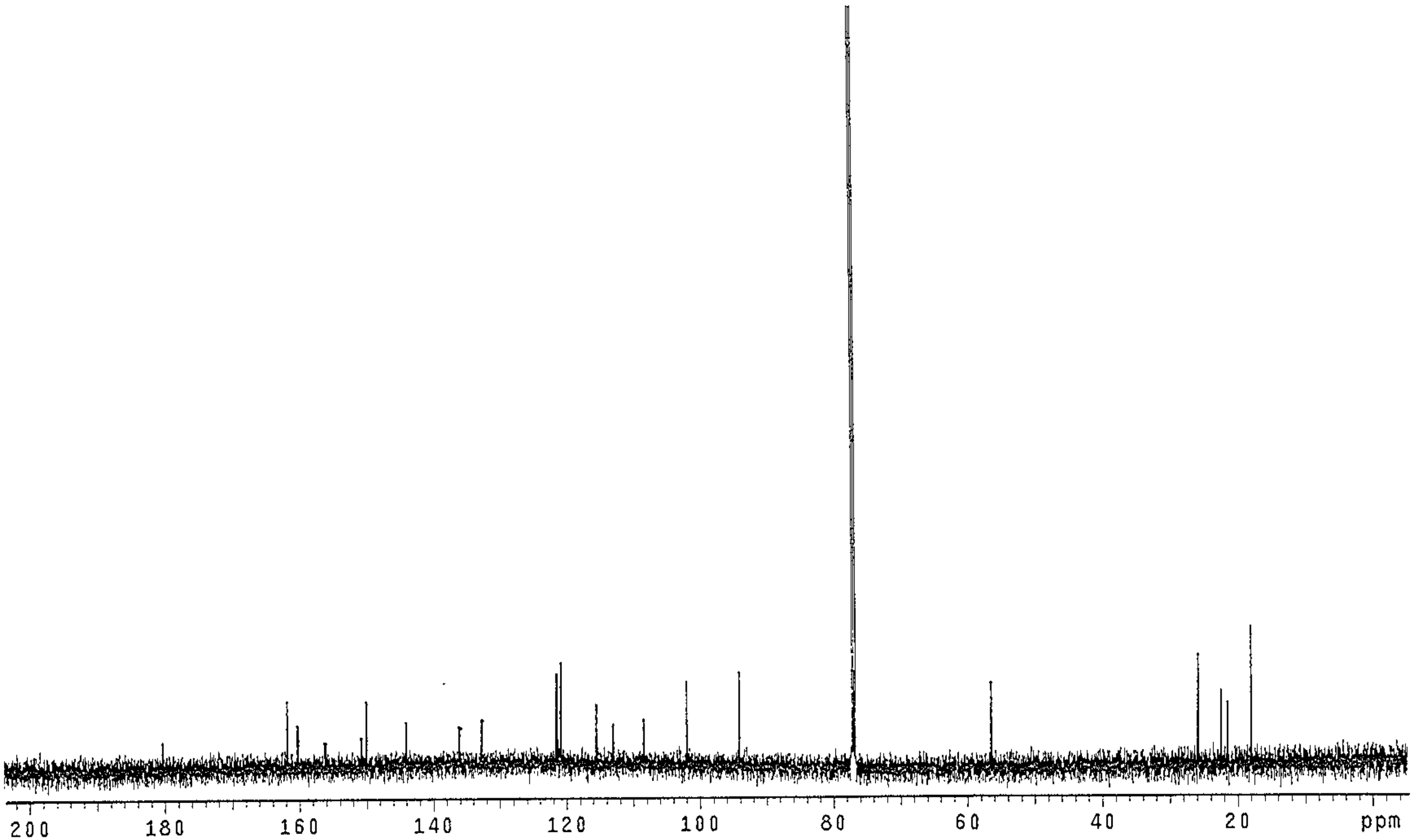


Figure 18 ^{13}C NMR (125 MHz)(CDCl$_3$) spectrum of **PGC4**

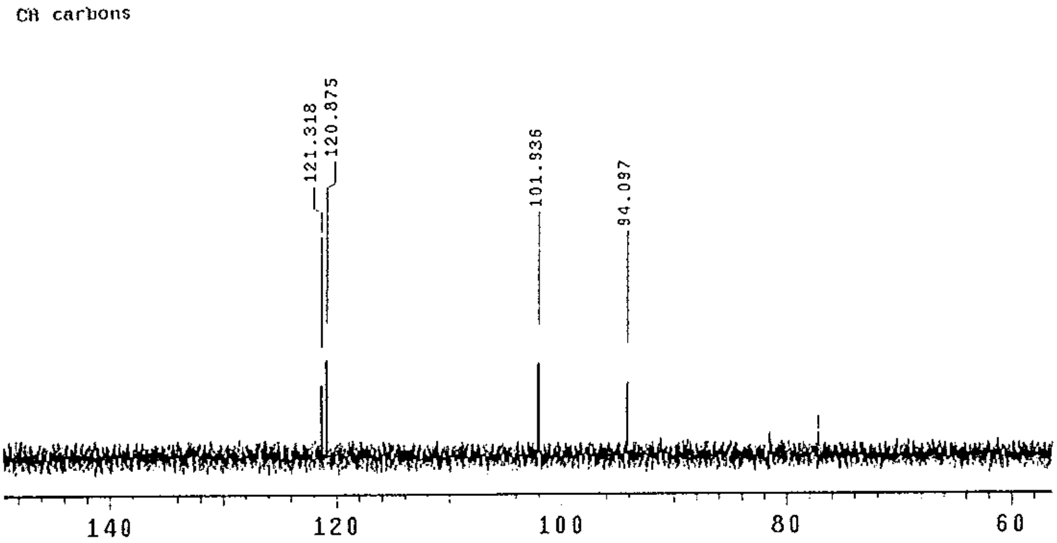


Figure 19 DEPT 90° spectrum of **PGC4**

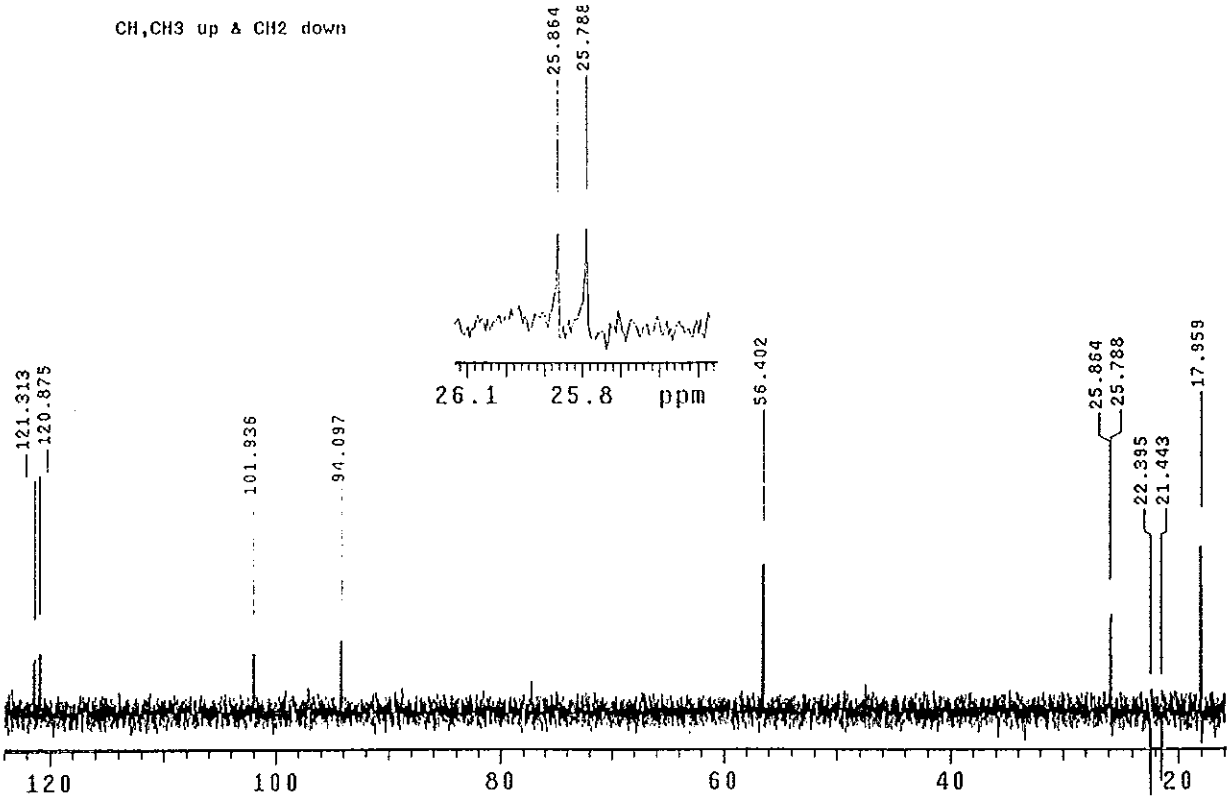


Figure 20 DEPT 135° spectrum of **PGC4**

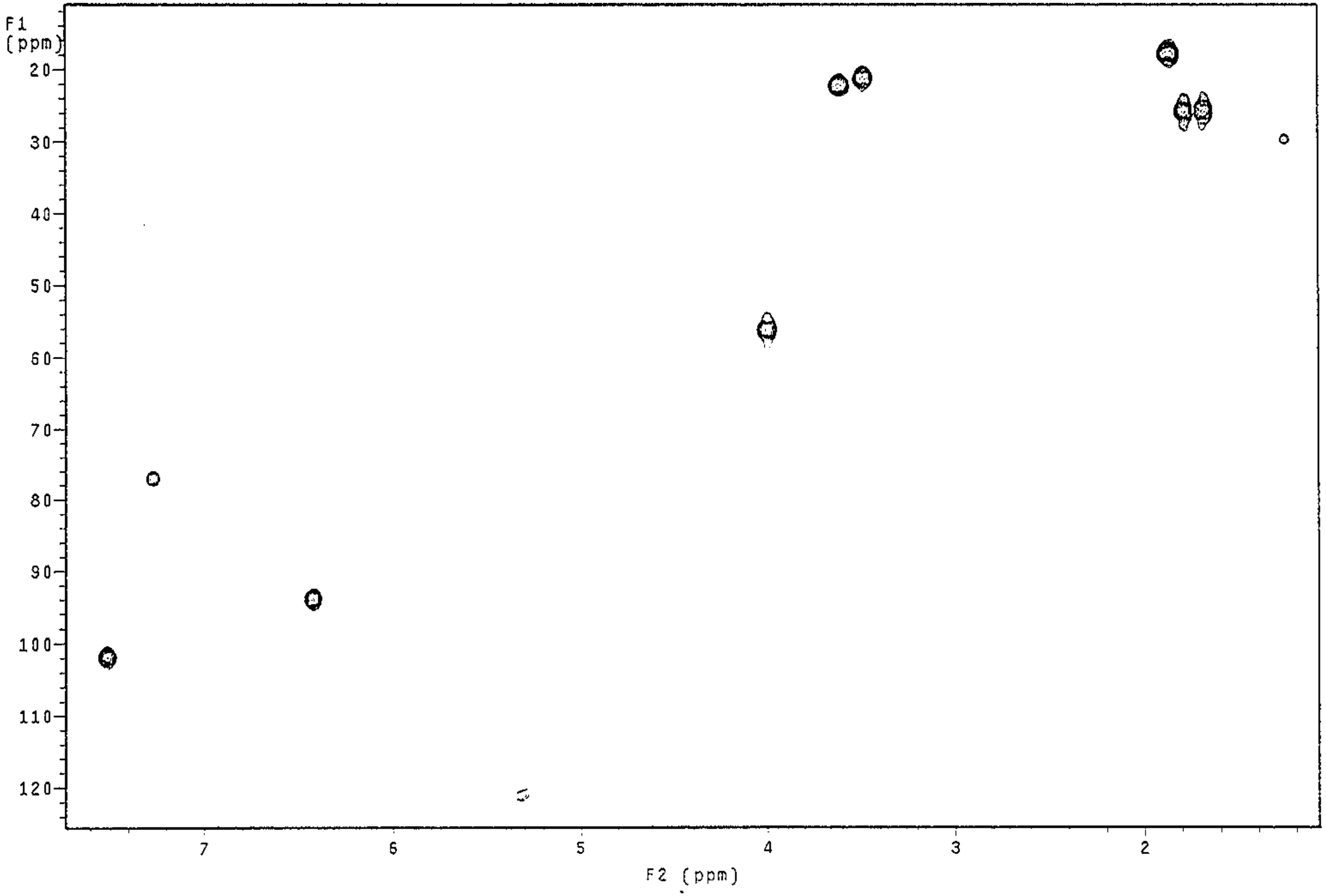


Figure 21 2D HMQC spectrum of **PGC4**

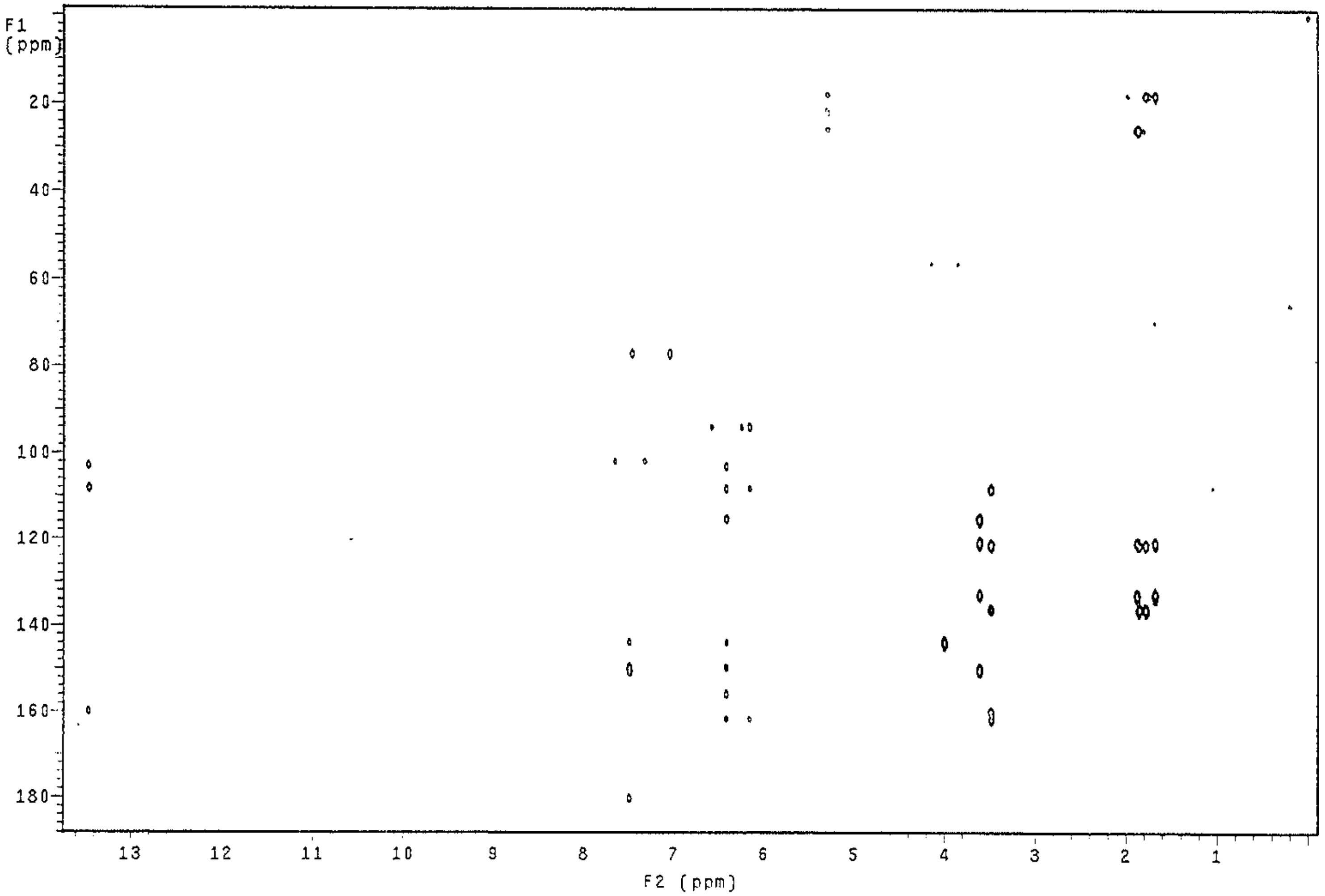


Figure 22 2D HMBC spectrum of **PGC4**

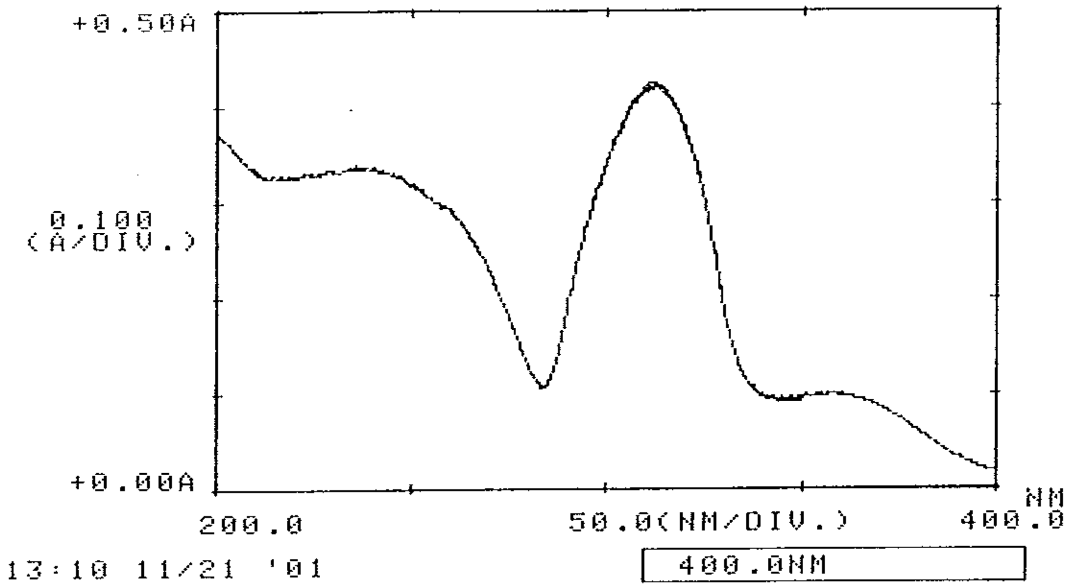


Figure 23 UV (EtOH) spectrum of **PGC5**

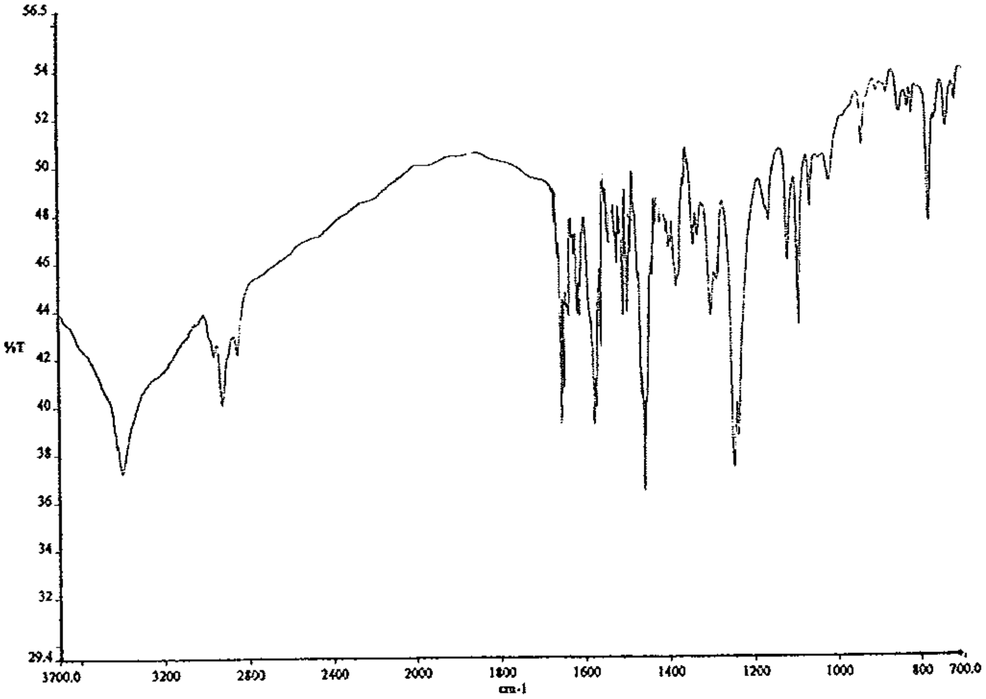


Figure 24 FT-IR (KBr) spectrum of **PGC5**

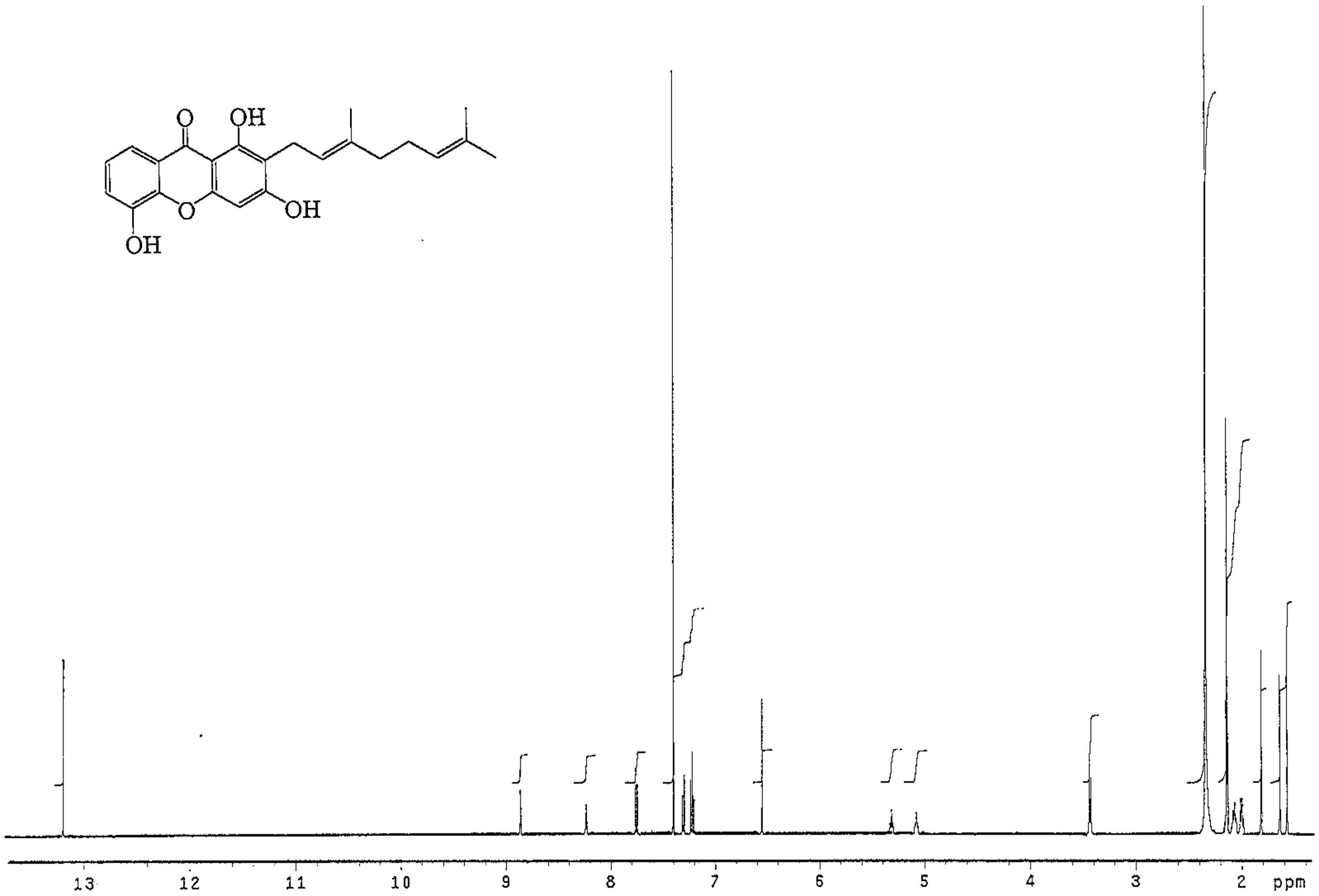


Figure 25 ^{1}H NMR (500 MHz)(CDCl$_3$+CD$_3$COCD$_3$) spectrum of **PGC5** (mangostinone)

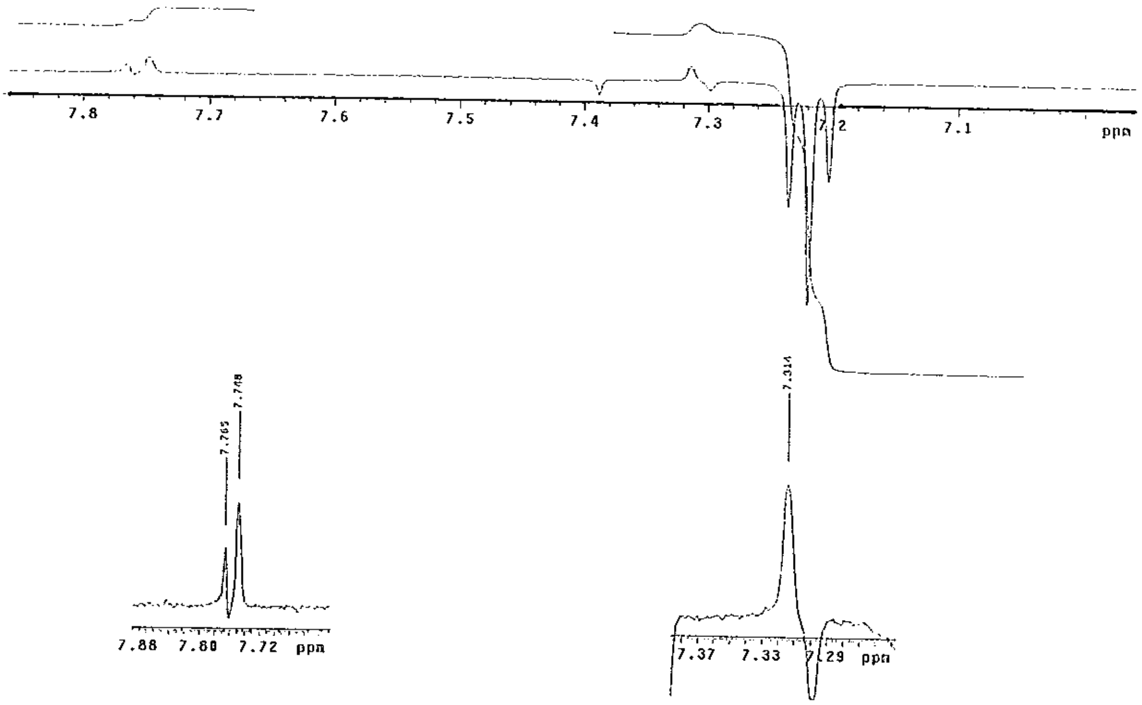


Figure 26 NOEDIFF spectrum of **PGC5** after irradiation at δ_H 7.22

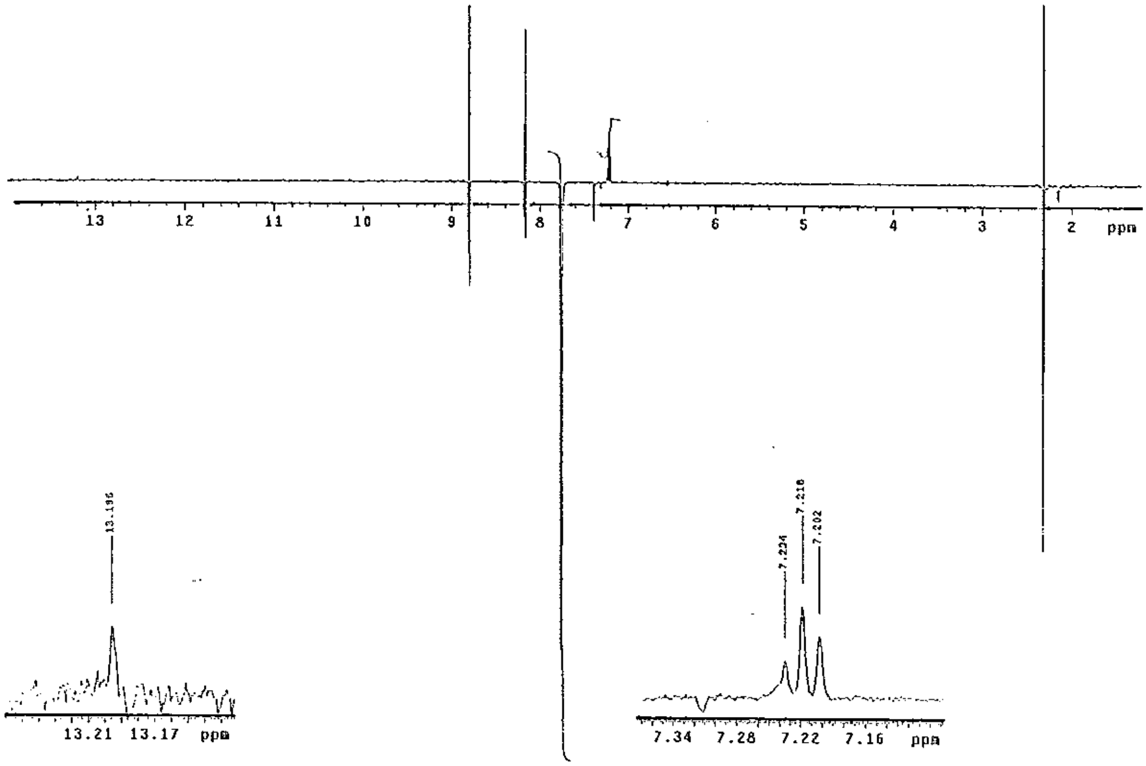


Figure 27 NOEDIFF spectrum of **PGC5** after irradiation at δ_H 7.76

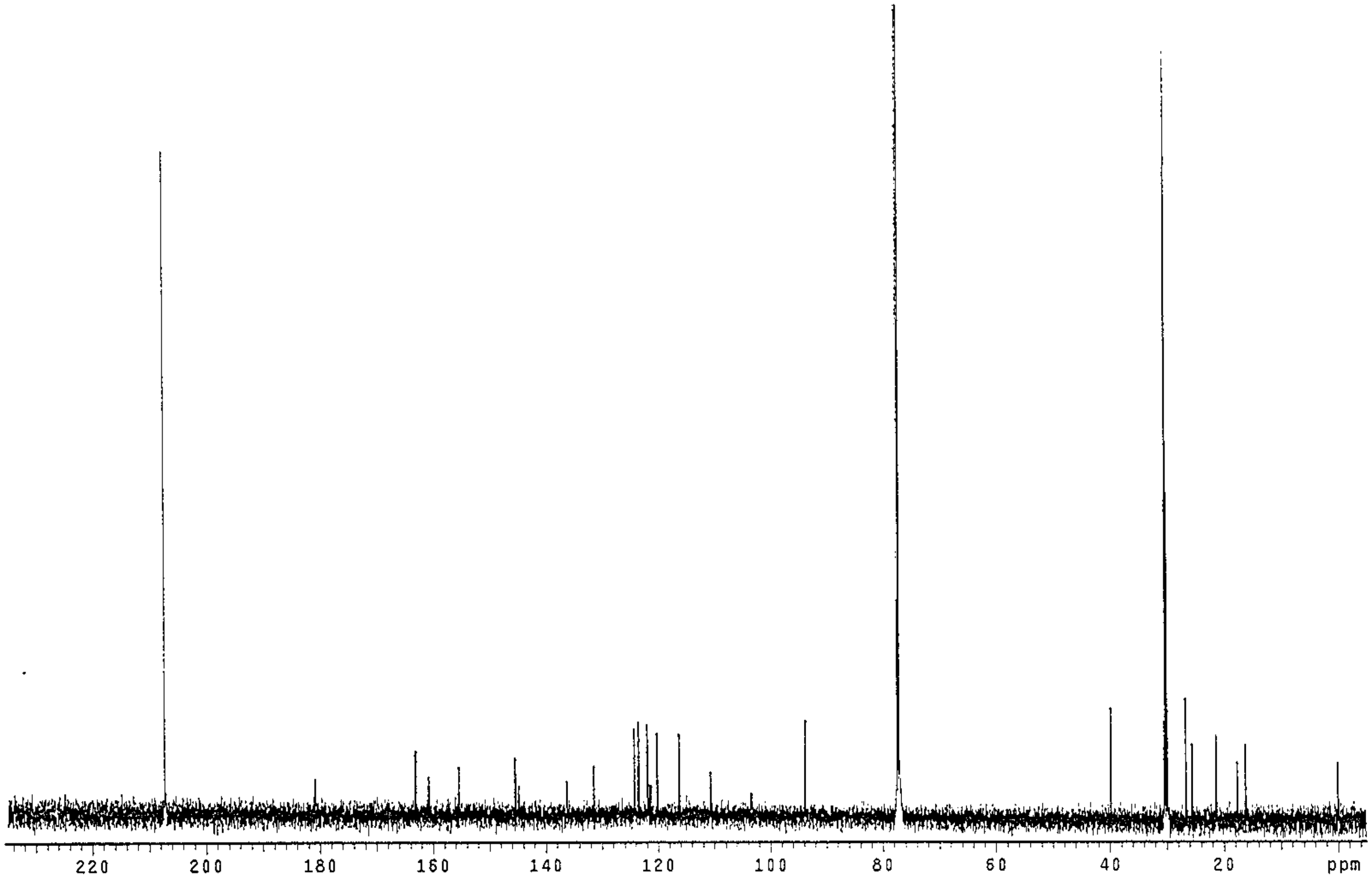


Figure 28 ^{13}C NMR (125 MHz)(CDCl$_3$+CD$_3$COCD$_3$) spectrum of **PGC5**

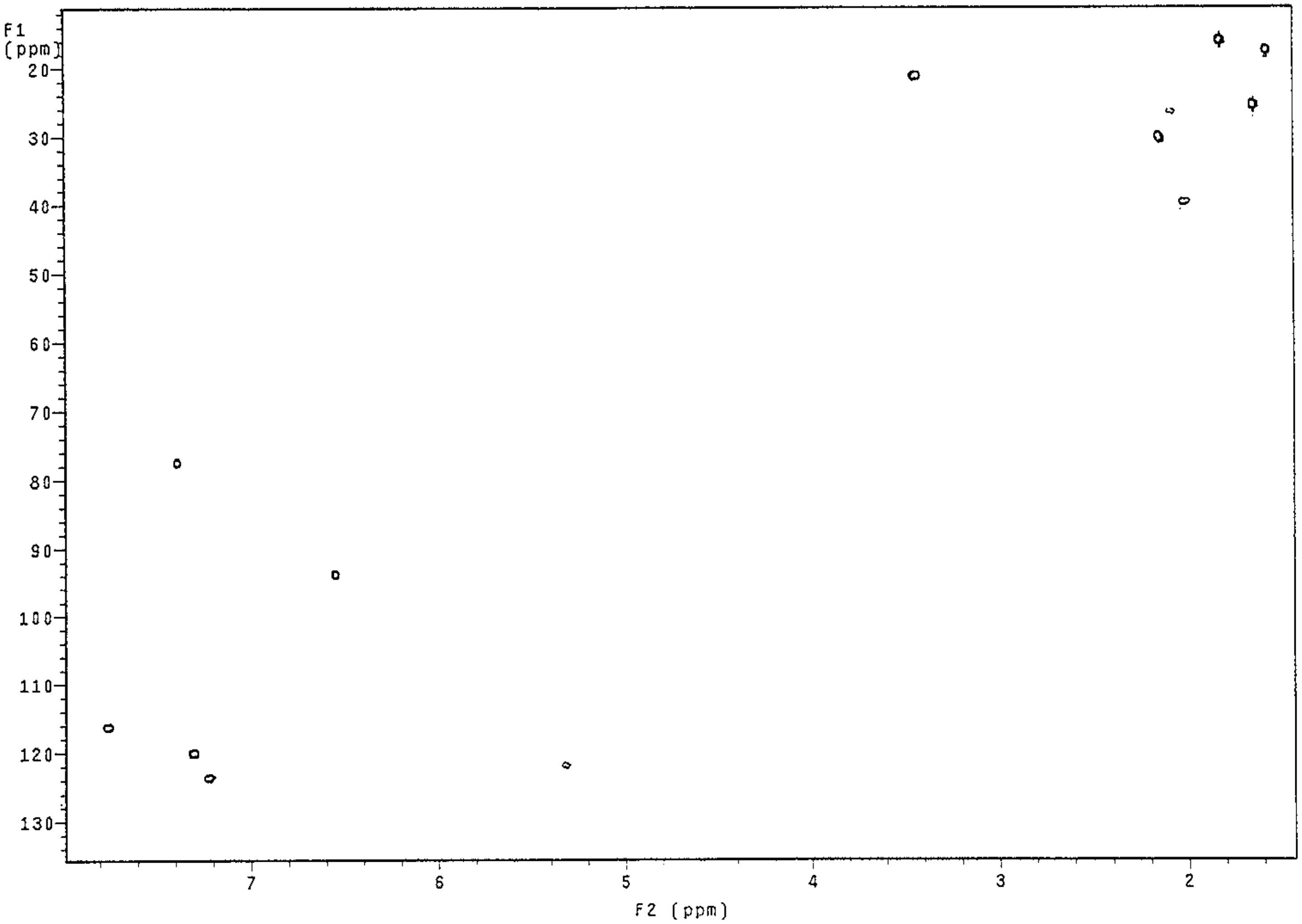


Figure 29 2D HMQC spectrum of **PGC5**

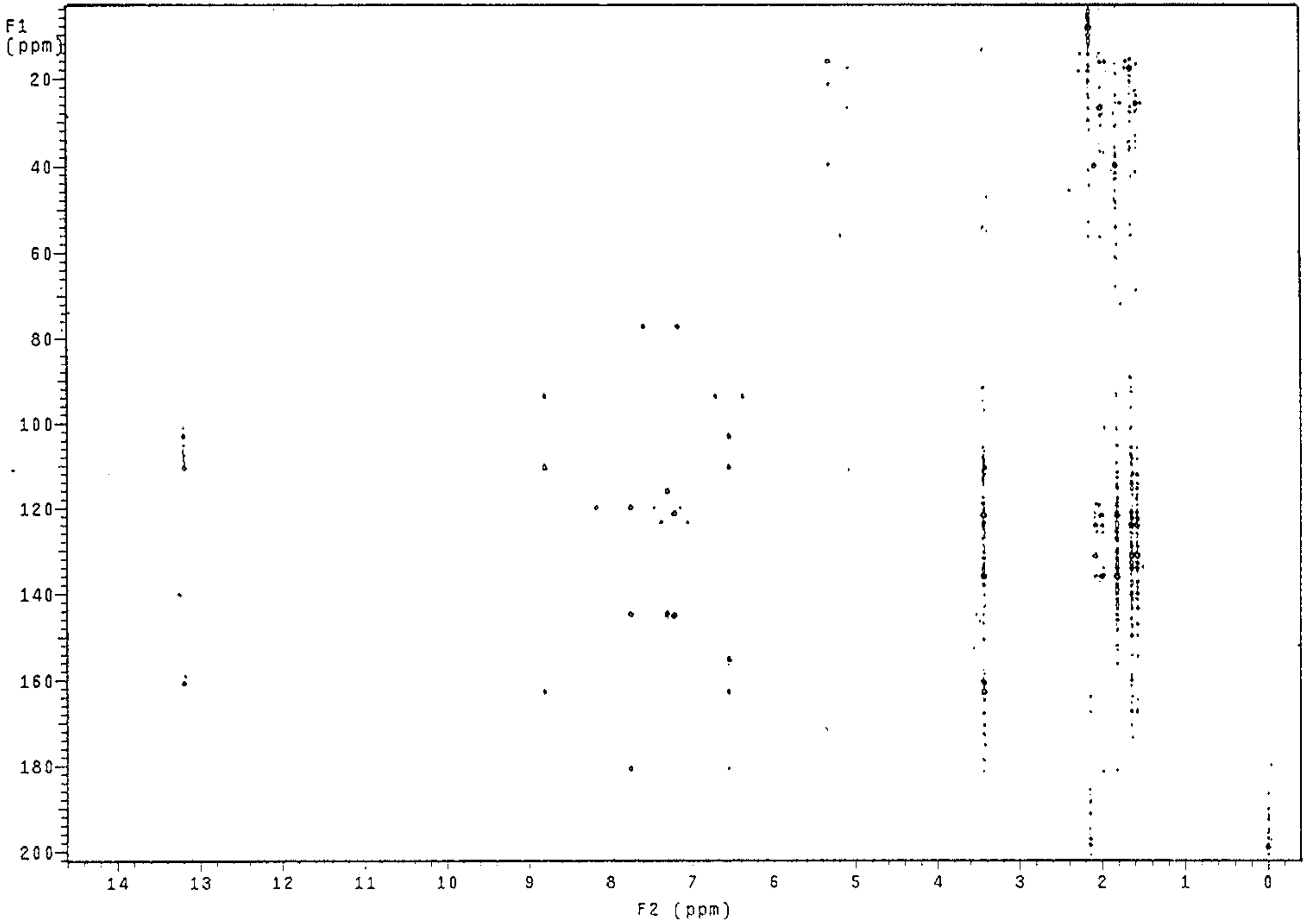


Figure 30 2D HMBC spectrum of **PGC5**

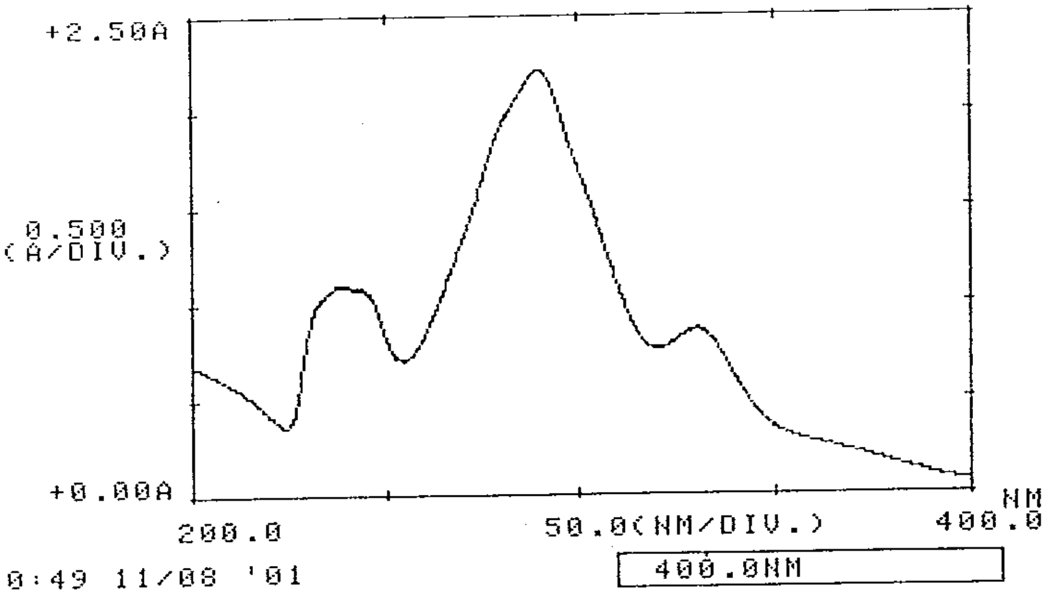


Figure 31 UV (EtOH) spectrum of **PGC6**

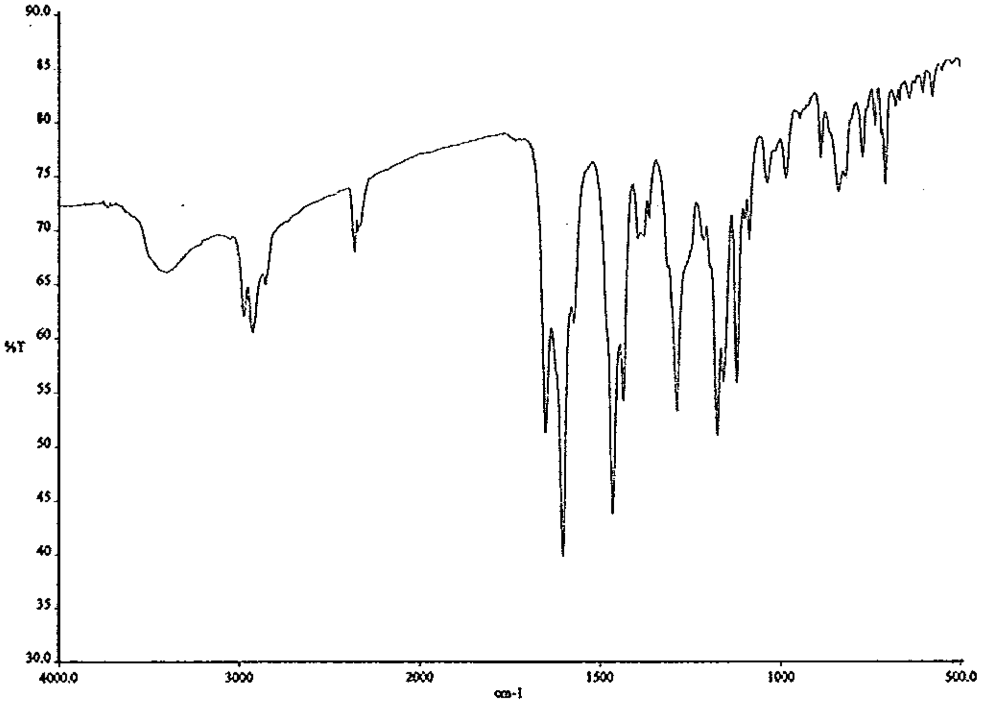


Figure 32 FT-IR (neat) spectrum of **PGC6**

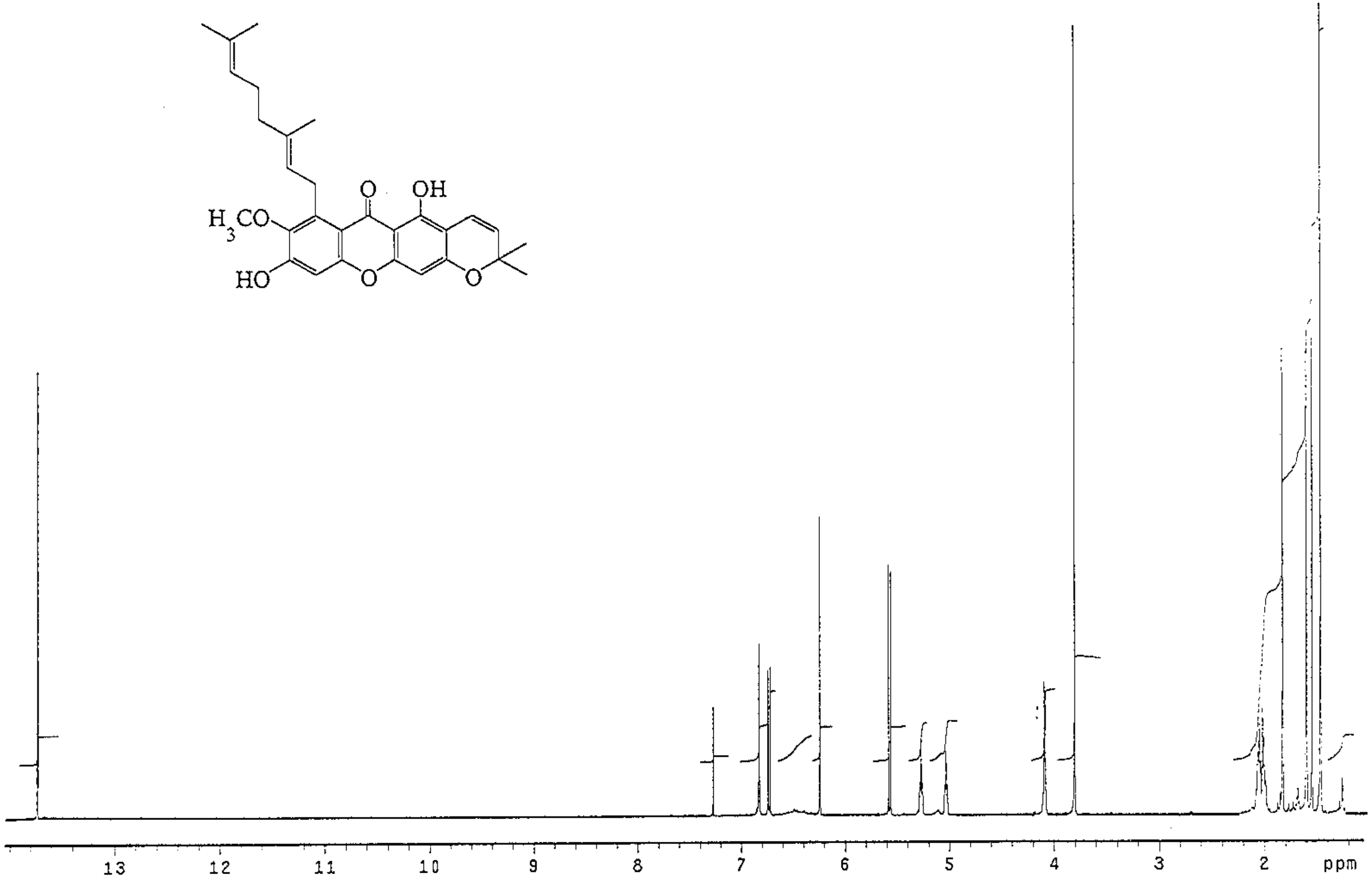


Figure 33 ^{1}H NMR (500 MHz)($CDCl_3$) spectrum of **PGC6**

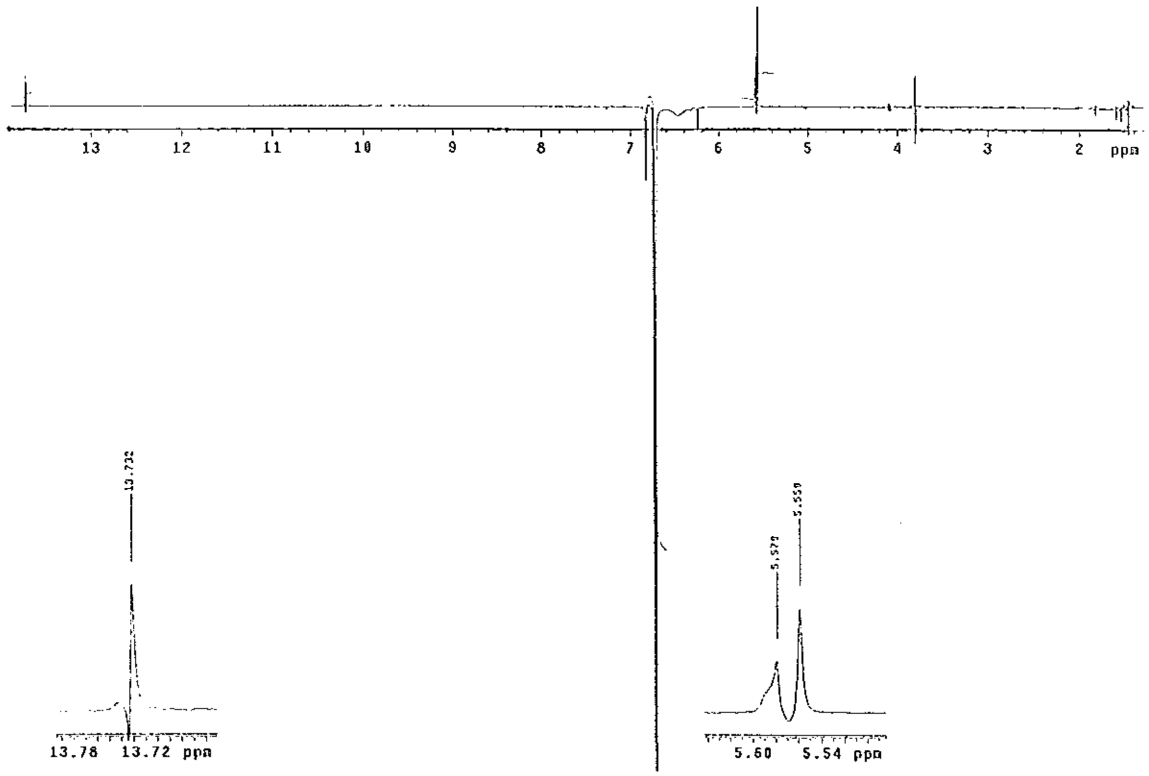


Figure 34 NOEDIFF spectrum of **PGC6** after irradiation at δ_H 6.73

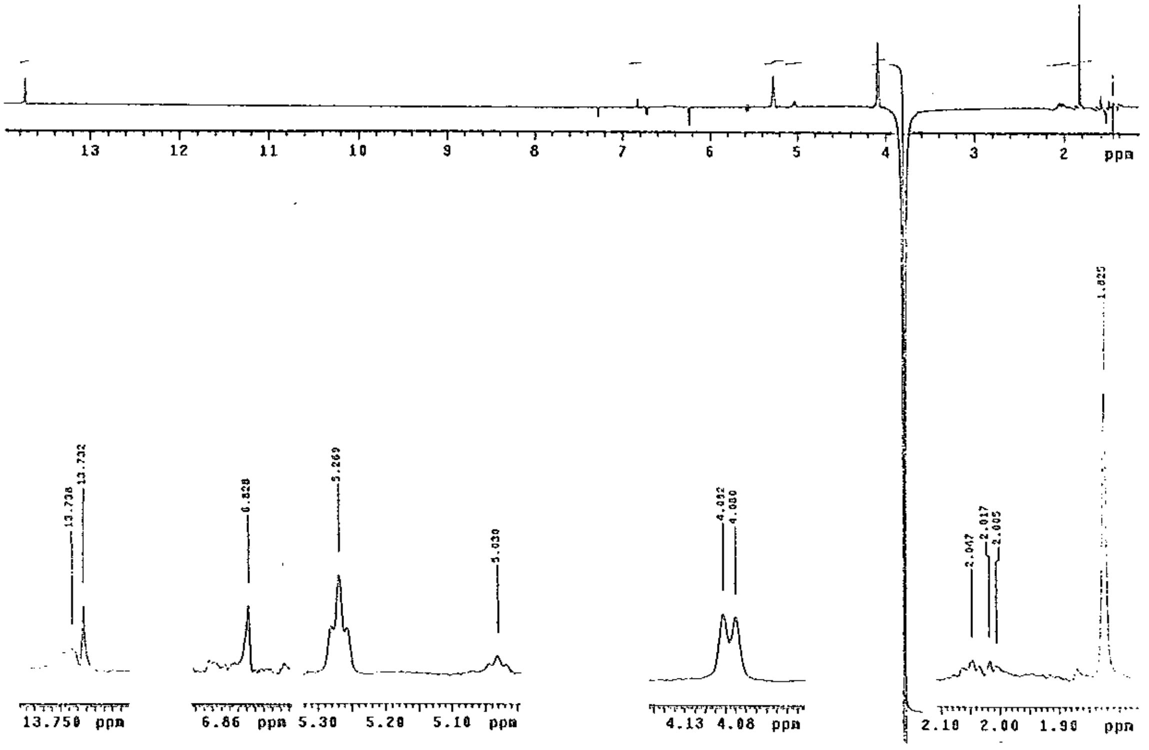


Figure 35 NOEDIFF spectrum of **PGC6** after irradiation at δ_H 3.80

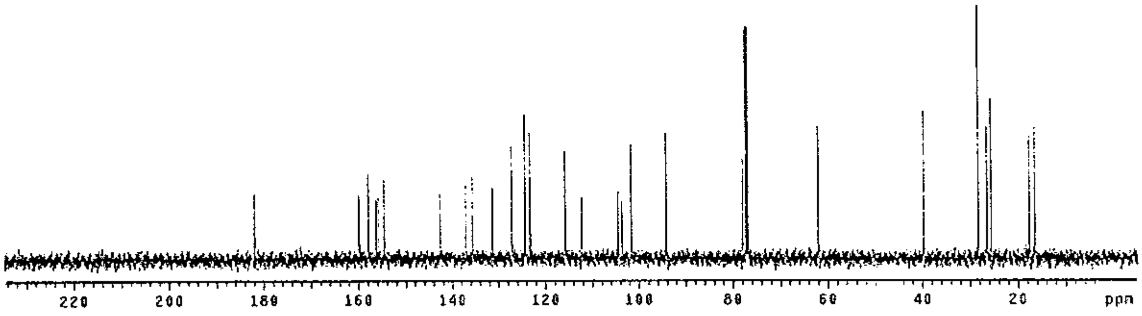


Figure 36 ^{13}C NMR (125 MHz)(CDCl$_3$) spectrum of **PGC6**

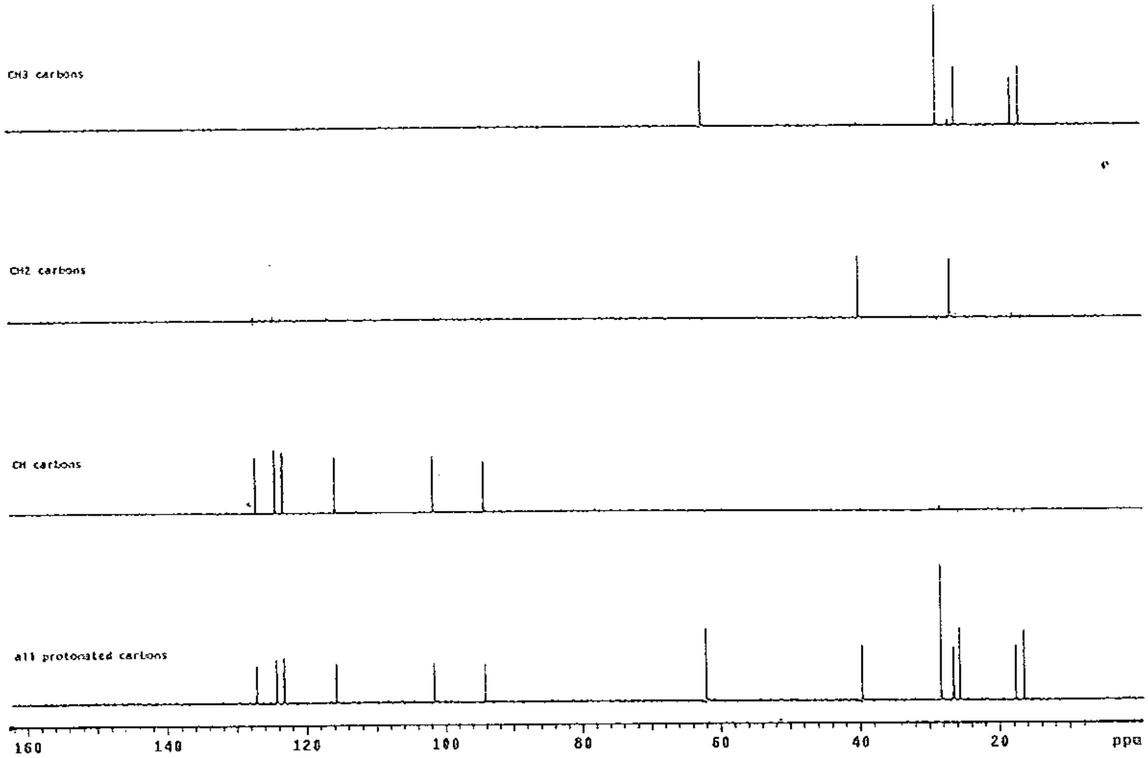


Figure 37 DEPT spectrum of **PGC6**

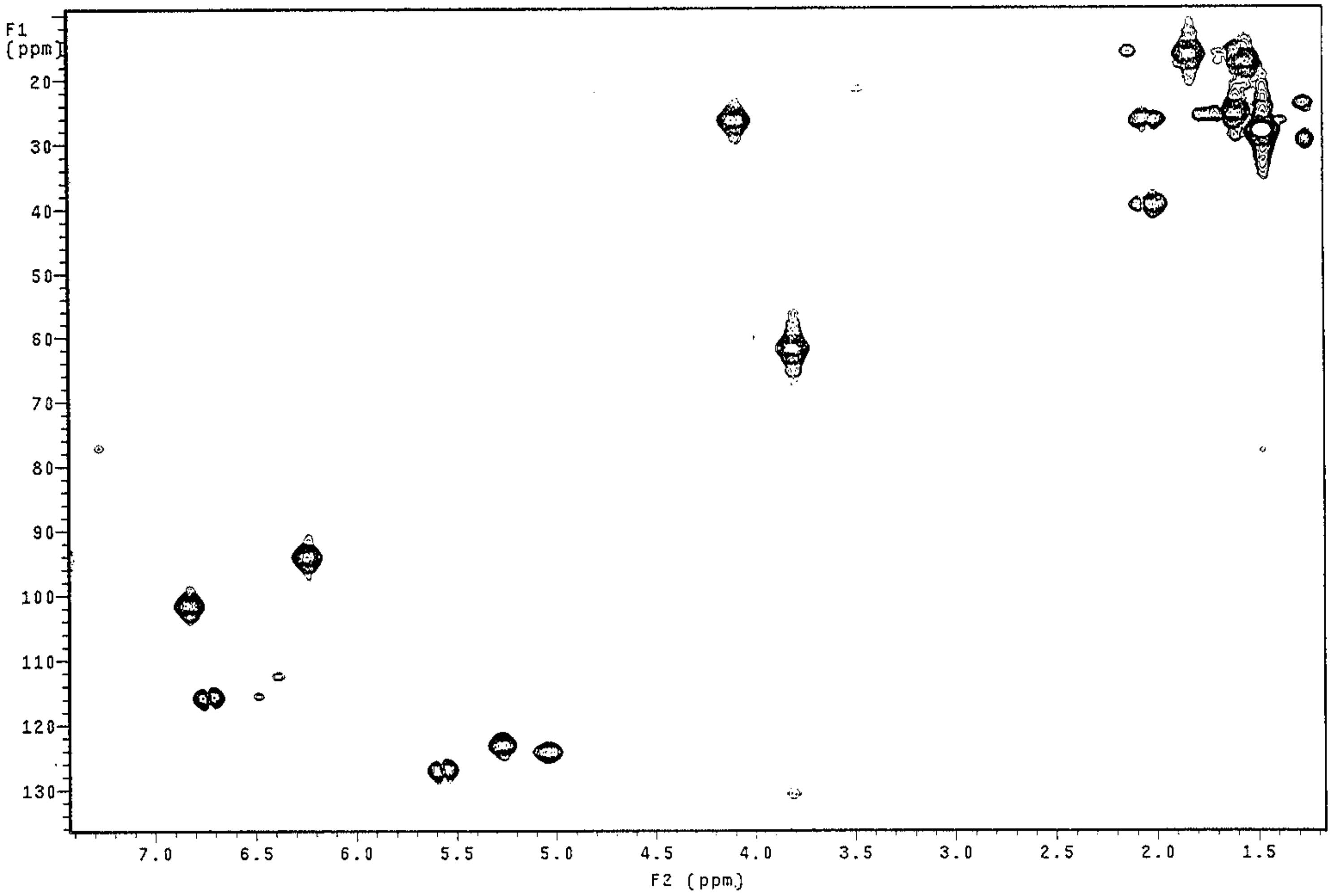


Figure 38 2D HMQC spectrum of **PGC6**

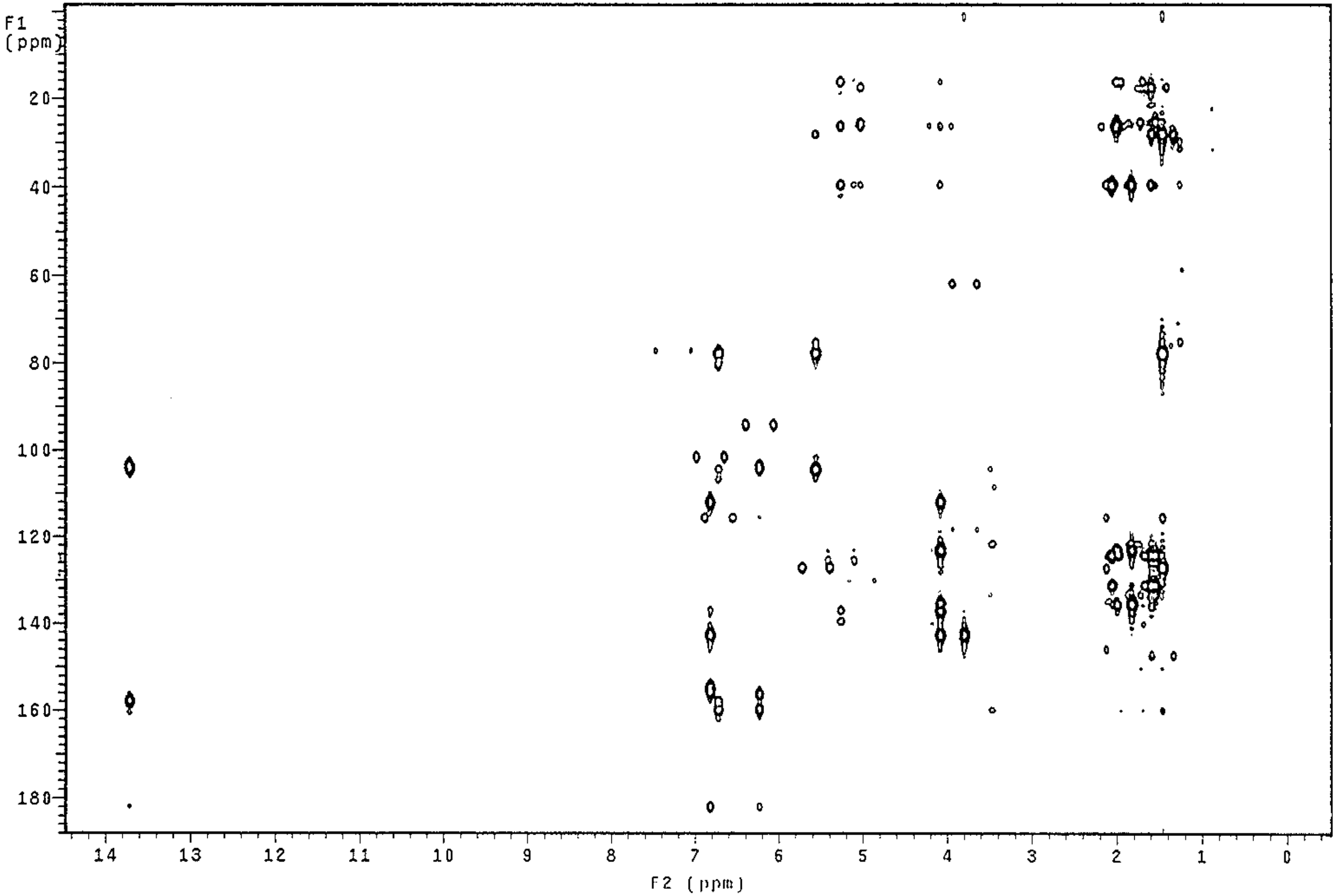


Figure 39 2D HMBC spectrum of **PGC6**

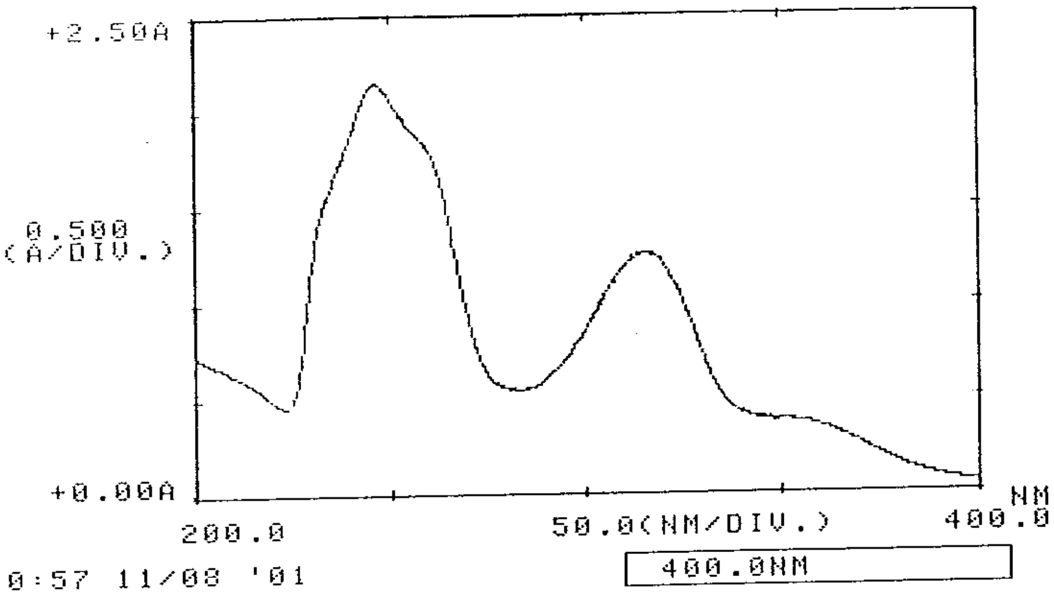


Figure 40 UV (EtOH) spectrum of **PGC7**

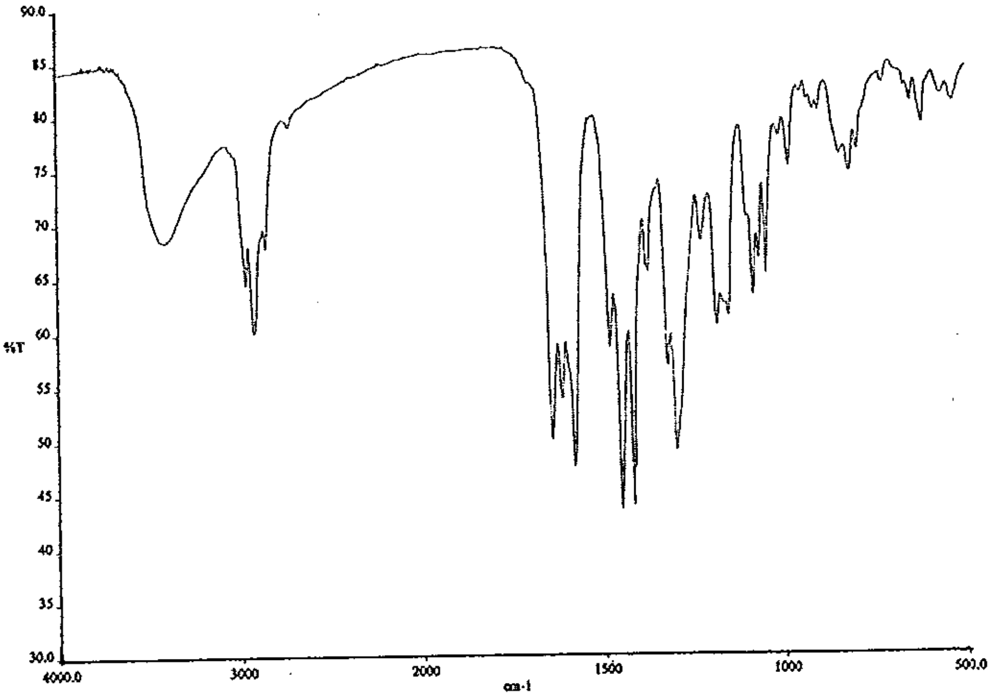


Figure 41 FT-IR (neat) spectrum of **PGC7**

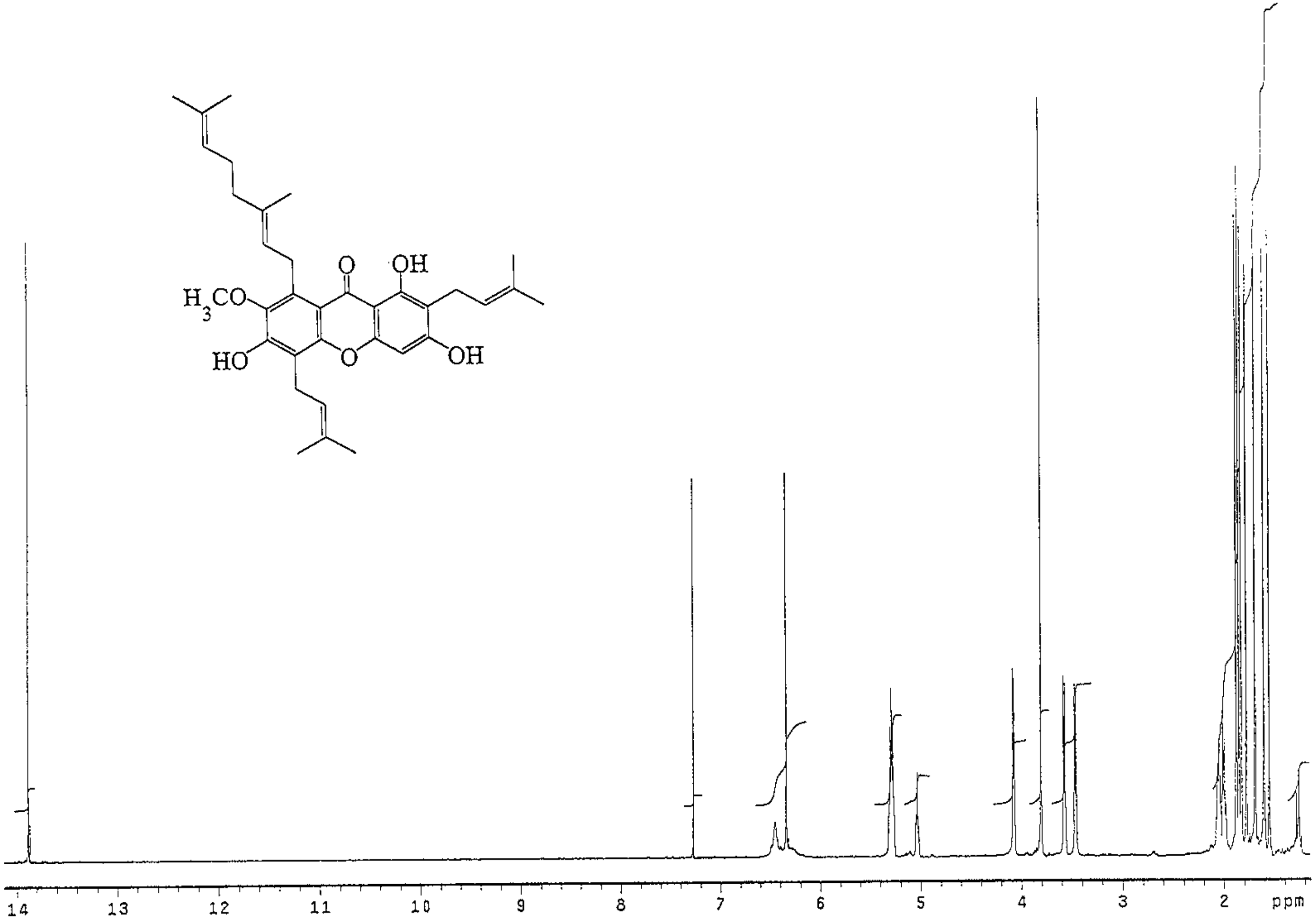


Figure 42 ^{1}H NMR (500 MHz)(CDCl$_3$) spectrum of **PGC7**

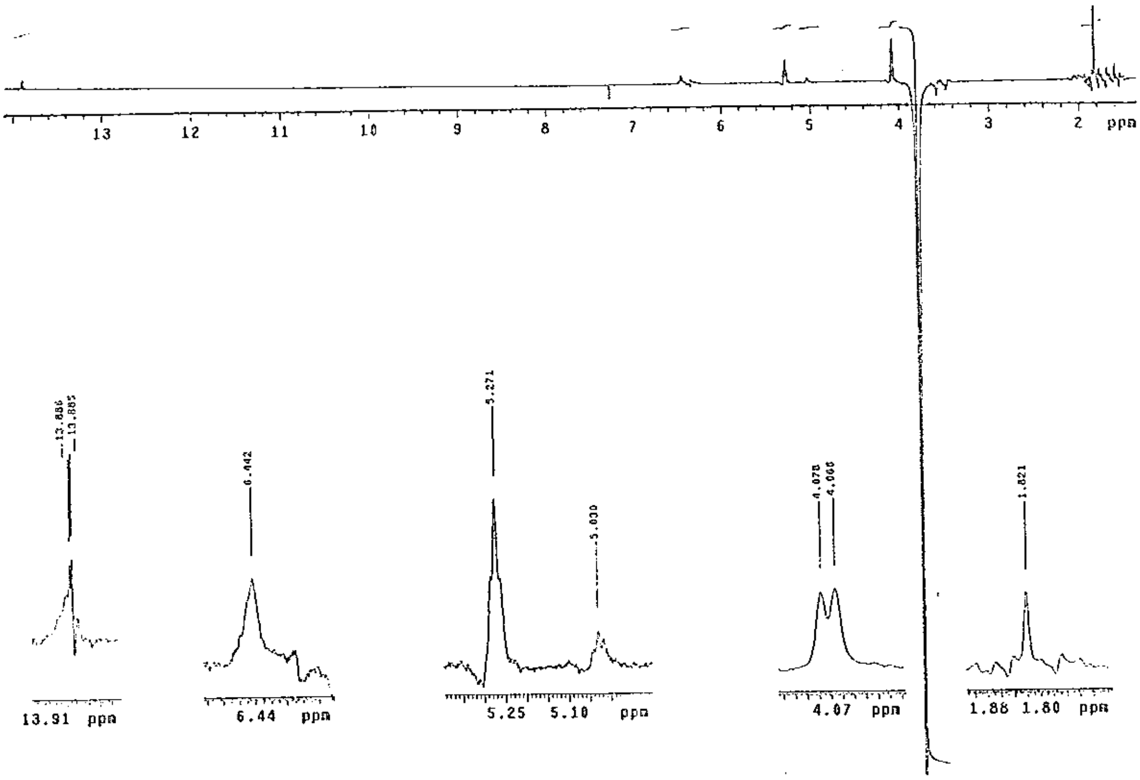


Figure 43 NOEDIFF spectrum of **PGC7** after irradiation at δ_H 3.80

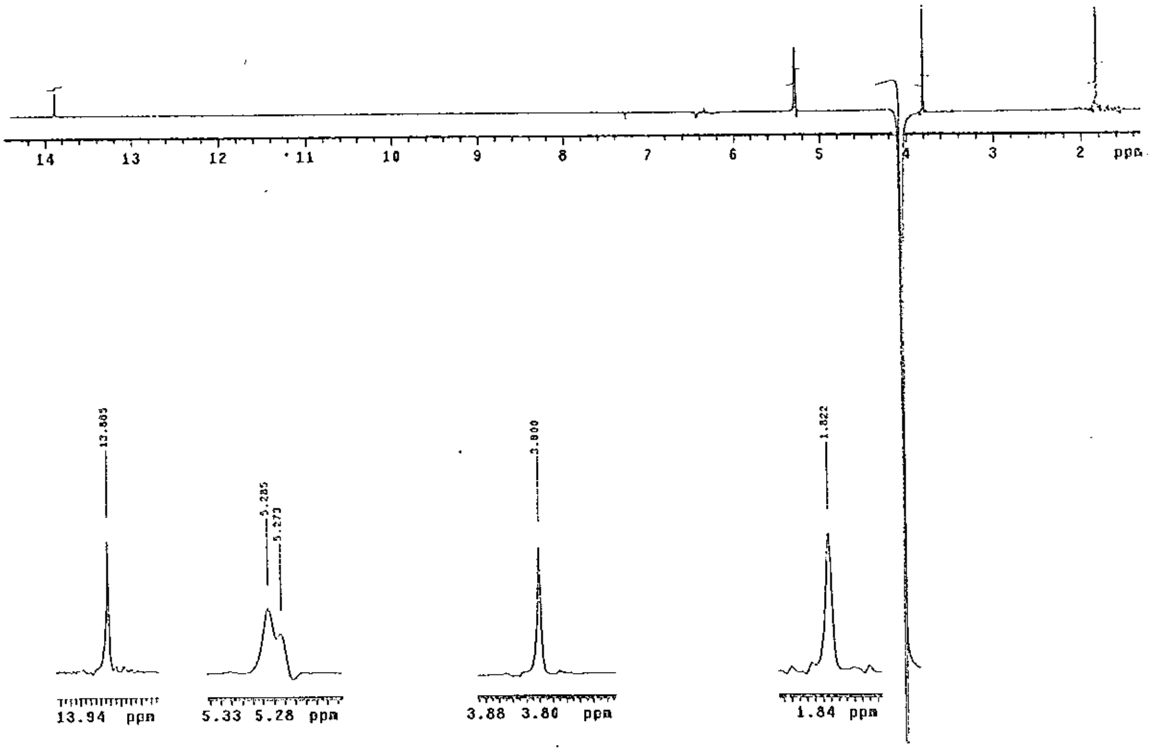


Figure 44 NOEDIFF spectrum of **PGC7** after irradiation at δ_H 4.09

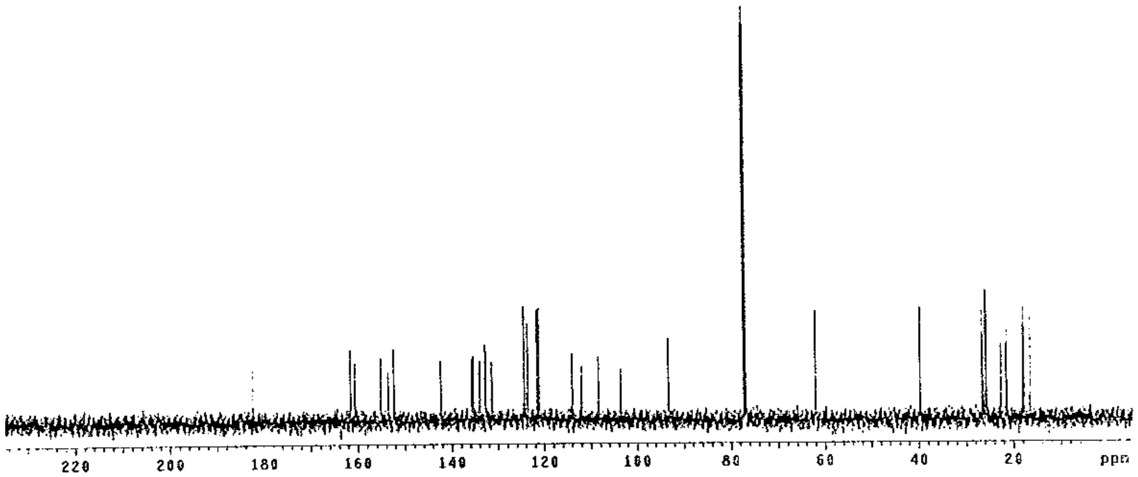


Figure 45 ^{13}C NMR (125 MHz)(CDCl$_3$) spectrum of **PGC7**

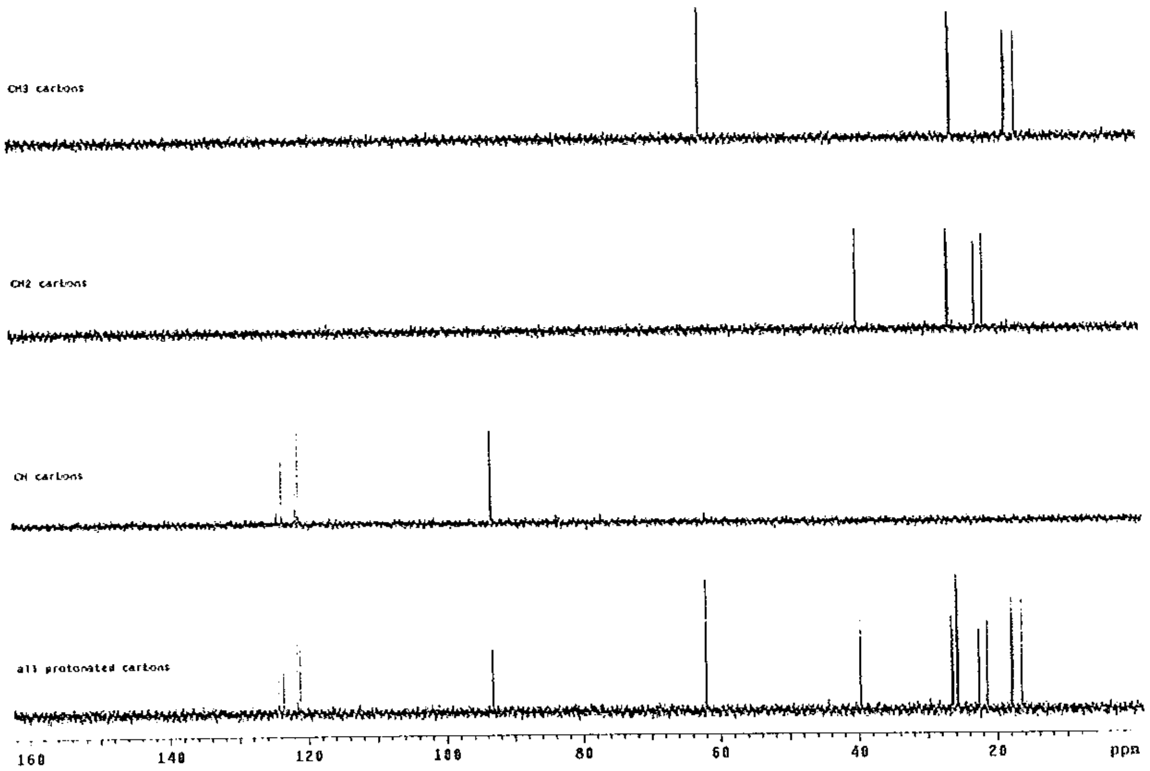


Figure 46 DEPT spectrum of **PGC7**

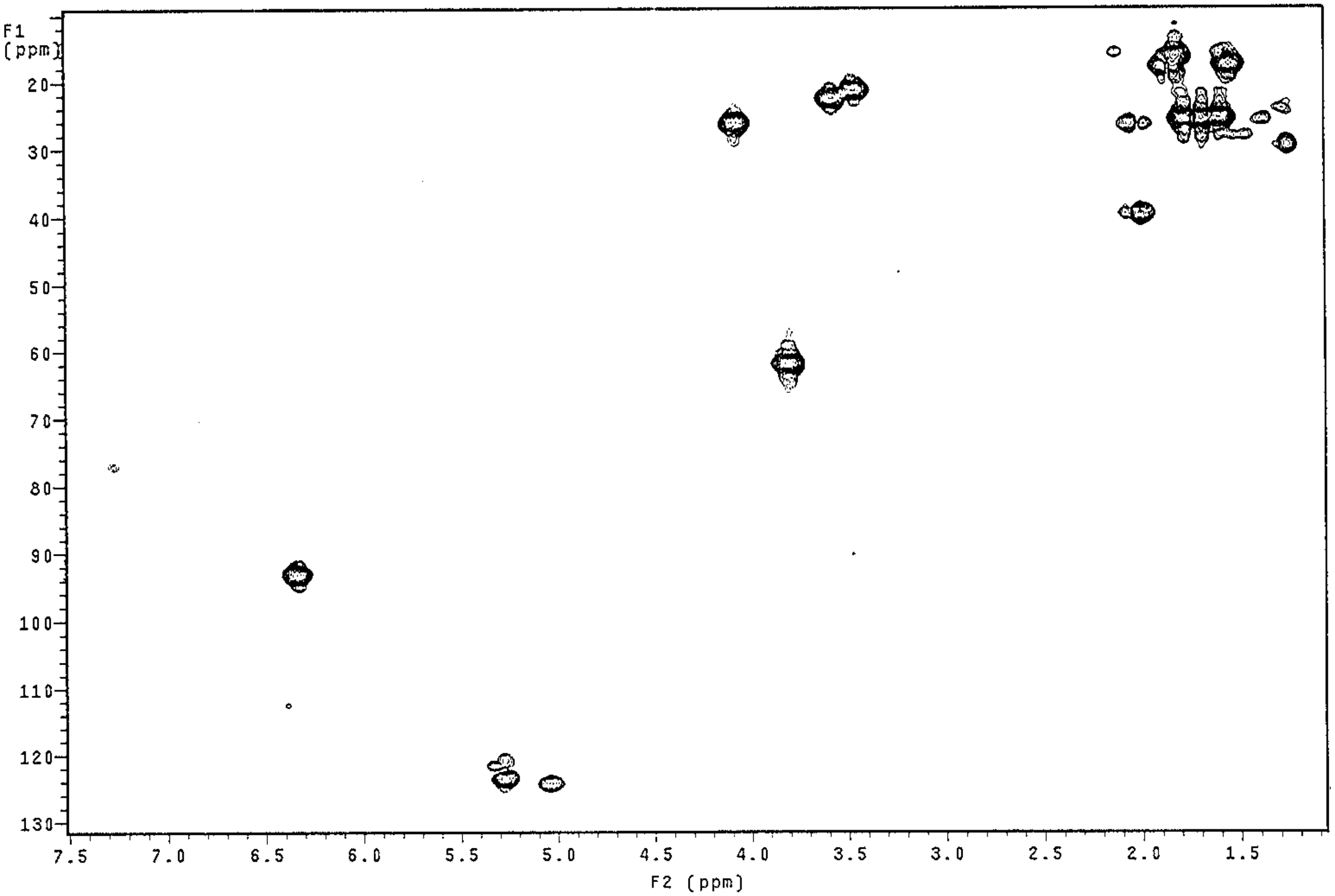


Figure 47 2D HMQC spectrum of **PGC7**

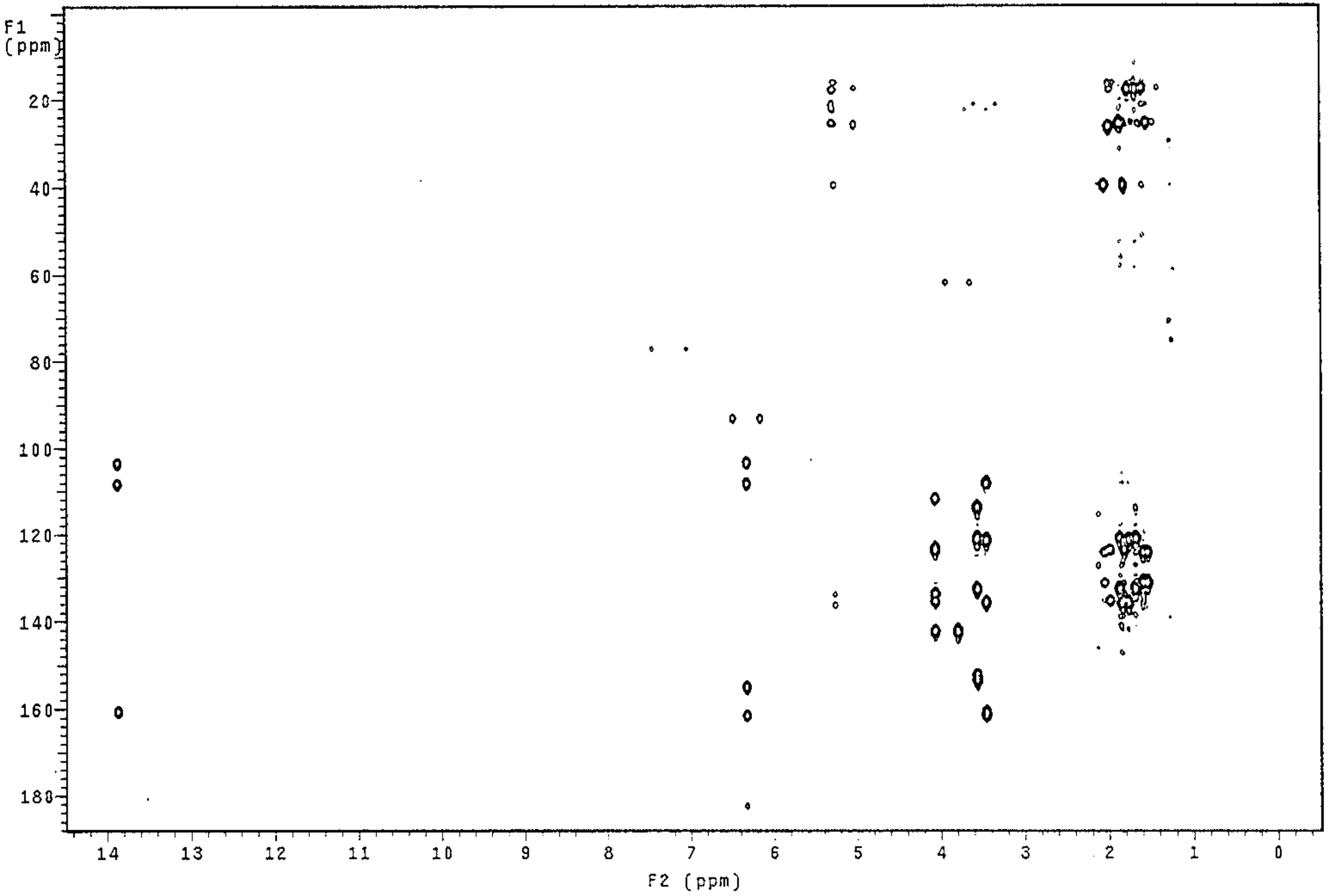


Figure 48 2D HMBC spectrum of **PGC7**

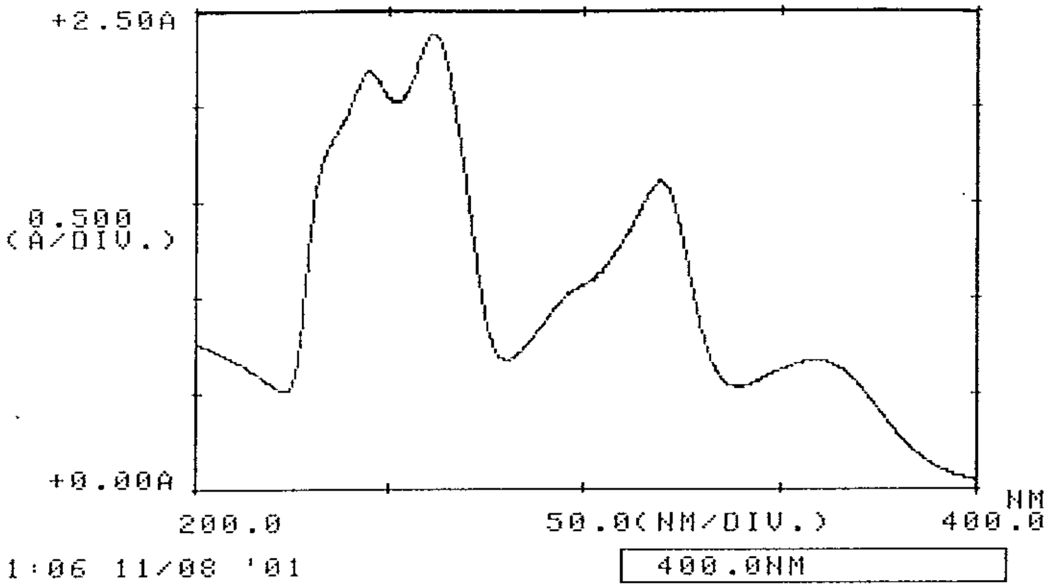


Figure 49 UV (EtOH) spectrum of **PGC8**

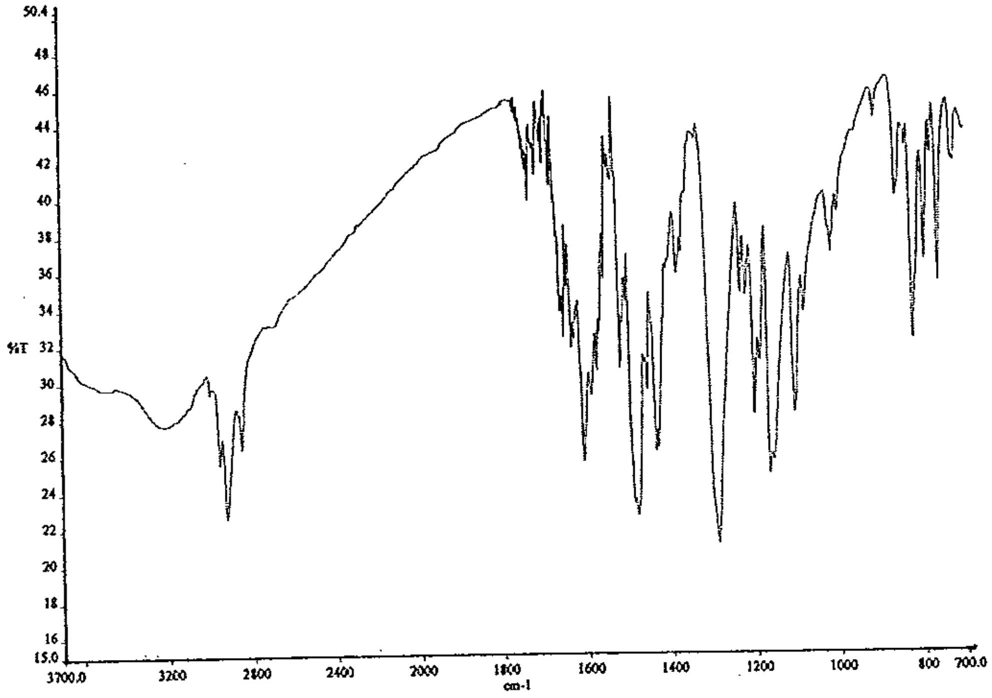


Figure 50 FT-IR (KBr) spectrum of **PGC8**

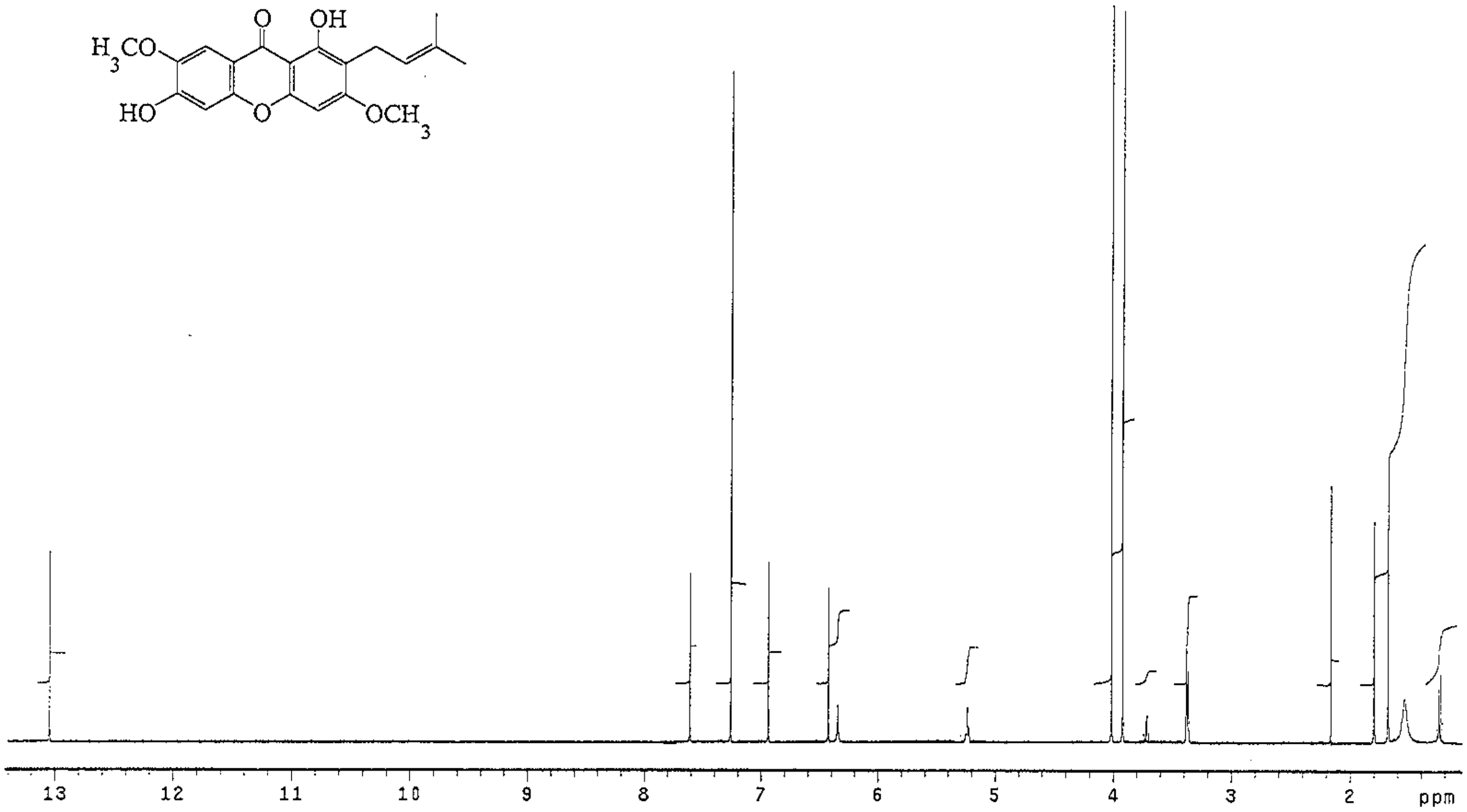


Figure 51 ^{1}H NMR (500 MHz)(CDCl$_3$) spectrum of **PGC8**

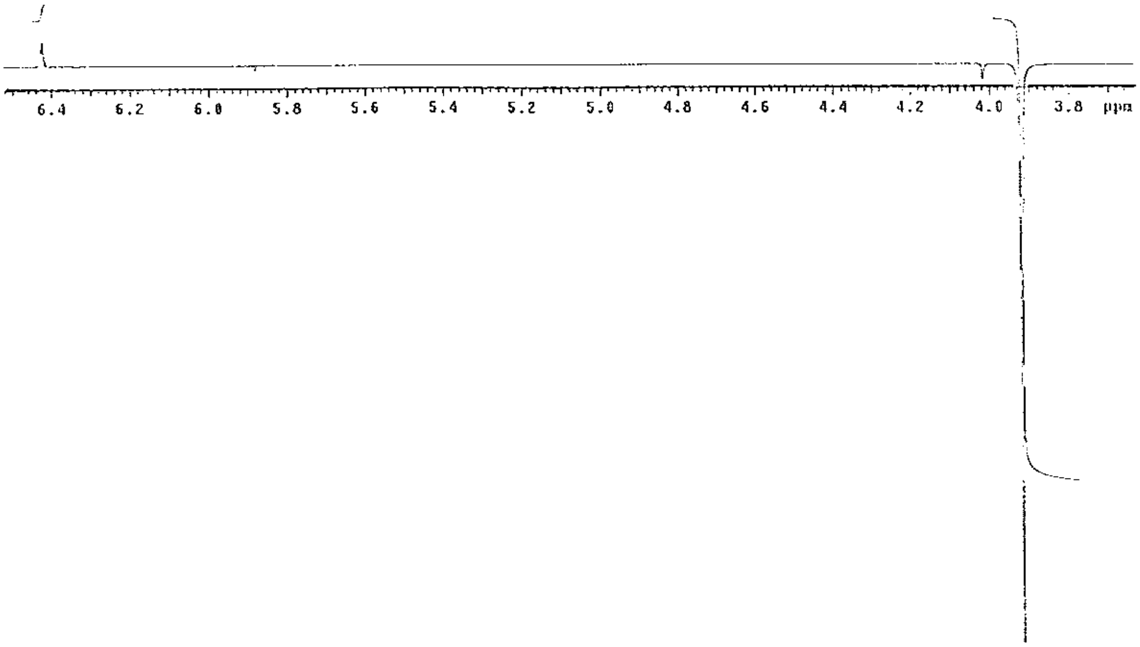


Figure 52 NOEDIFF spectrum of **PGC8** after irradiation at δ_H 3.92

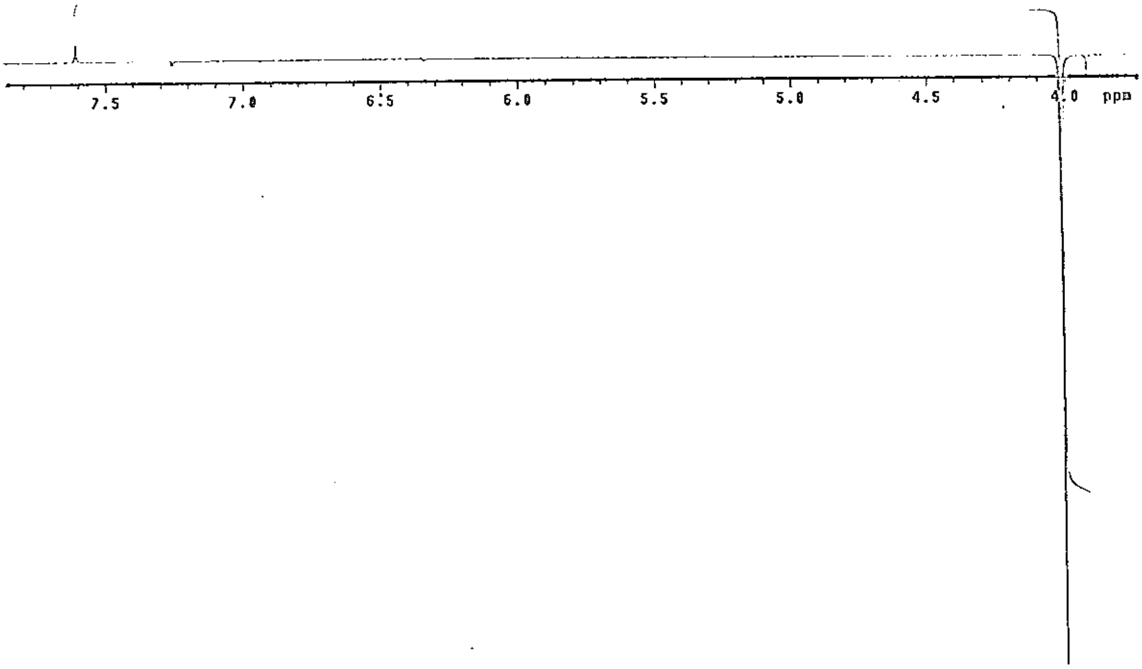


Figure 53 NOEDIFF spectrum of **PGC8** after irradiation at δ_H 4.02

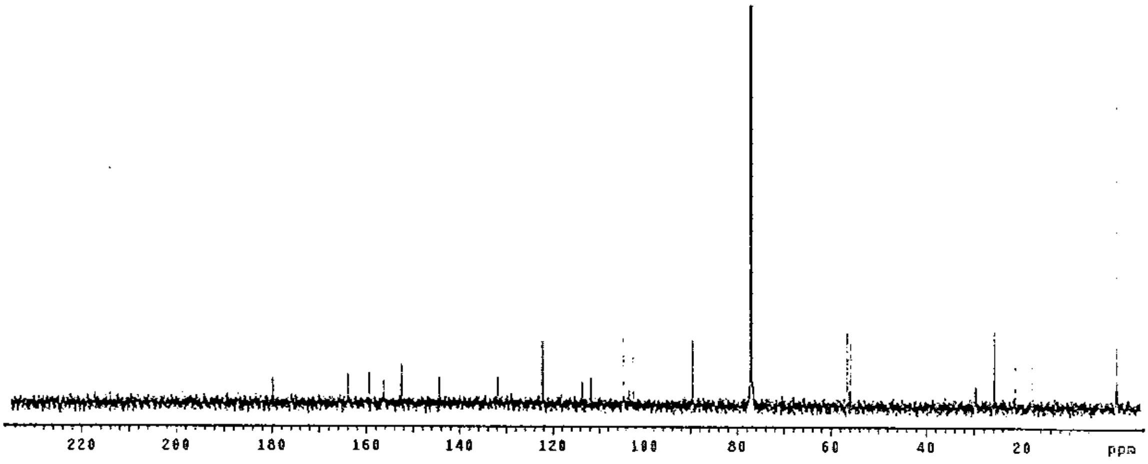


Figure 54 ^{13}C NMR (125 MHz)(CDCl$_3$) spectrum of **PGC8**

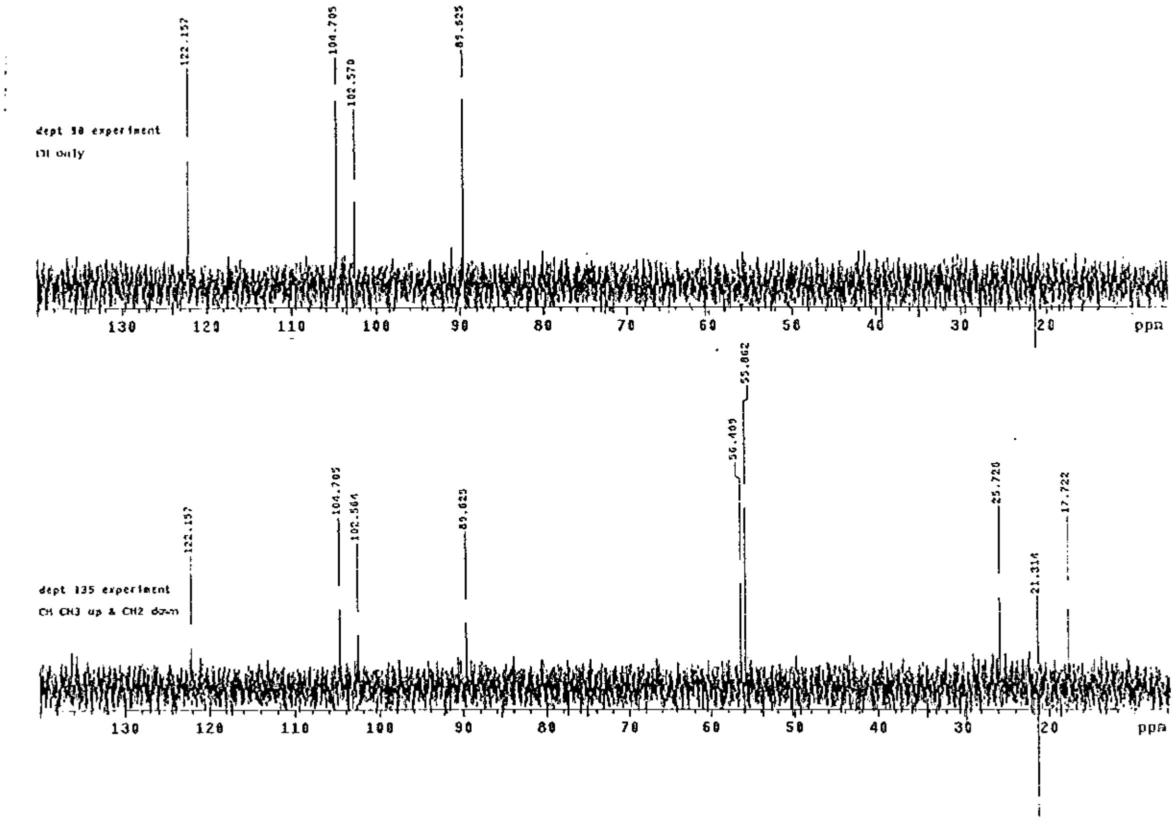


Figure 55 DEPT spectrum of **PGC8**

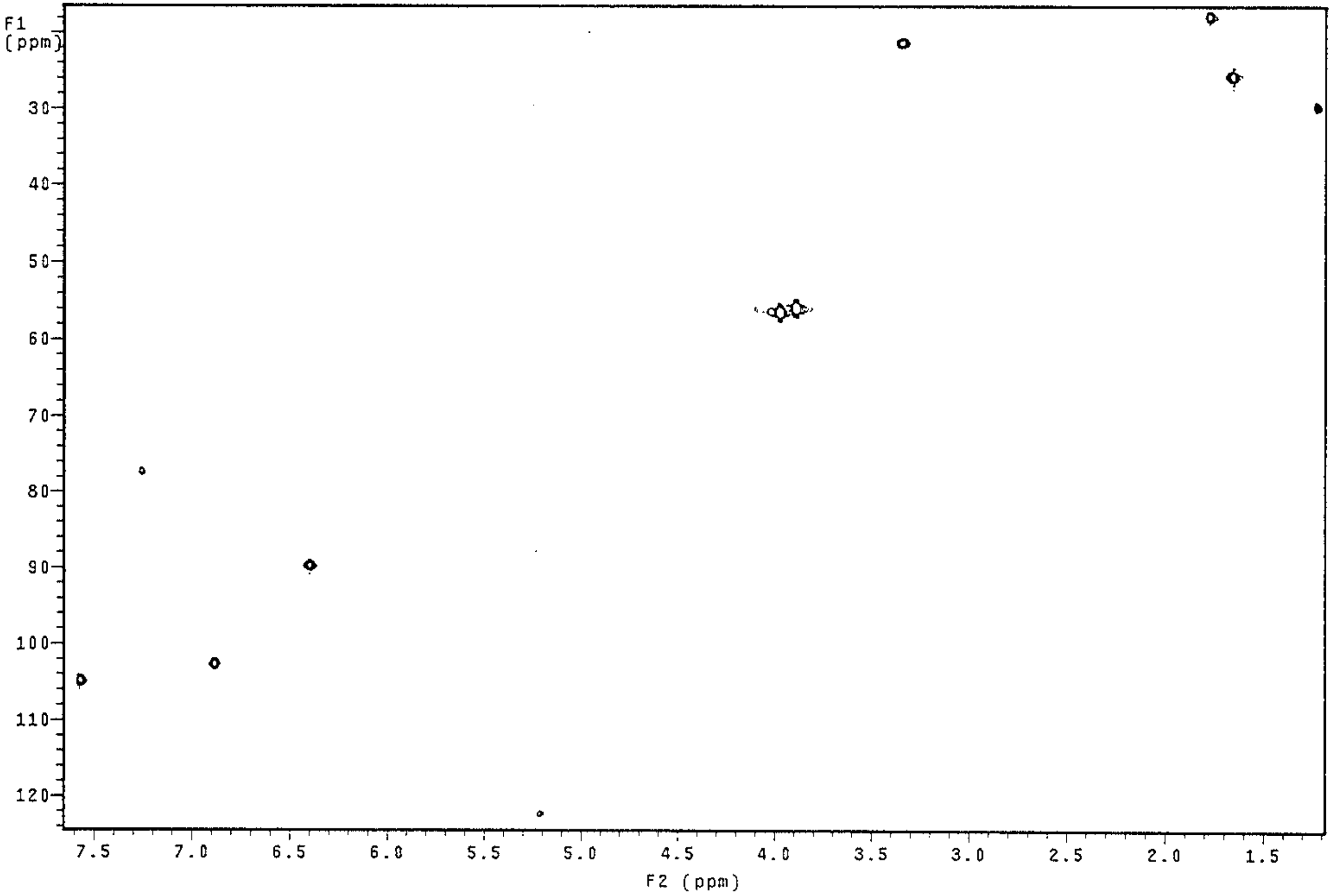


Figure 56 2D HMQC spectrum of **PGC8**

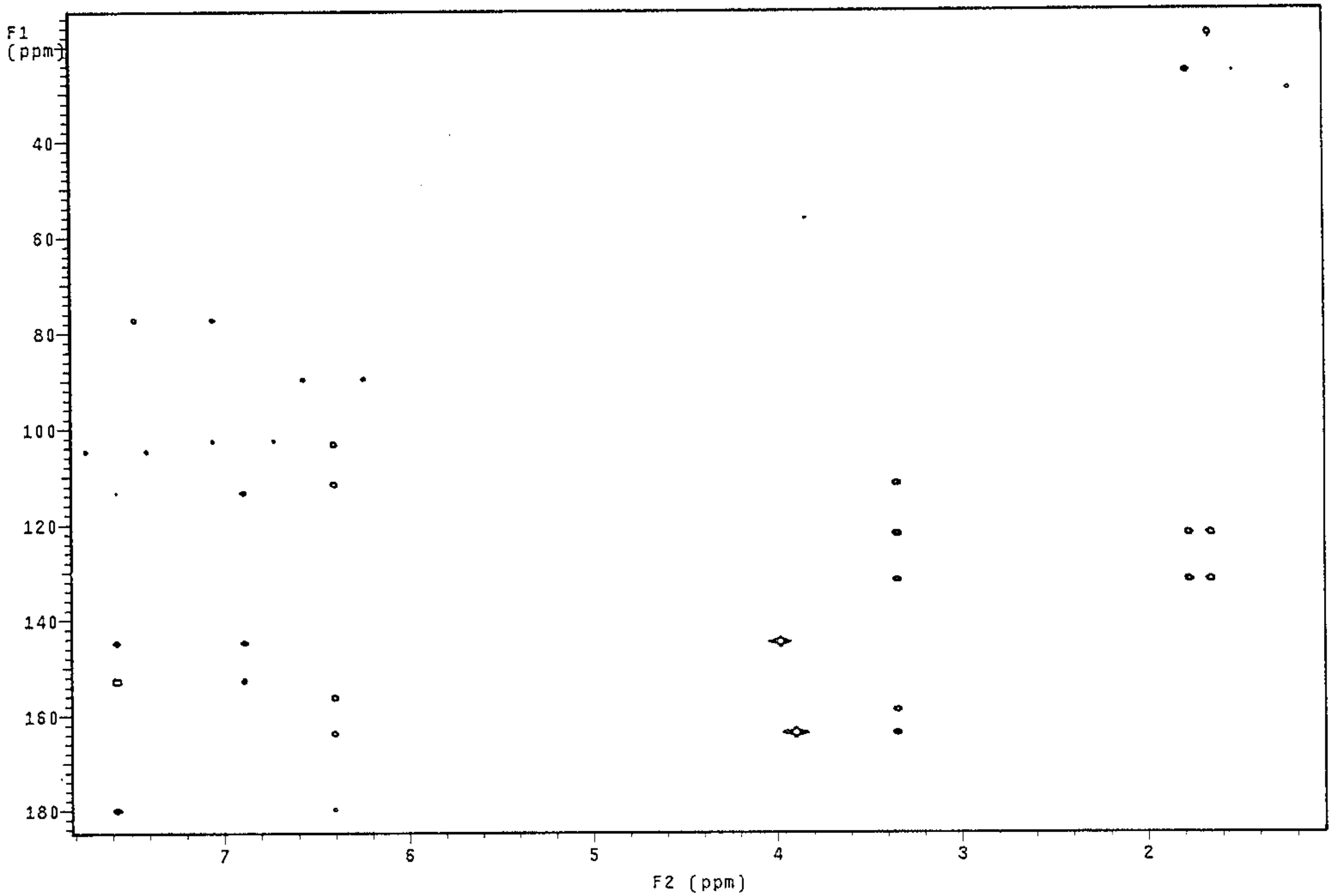


Figure 57 2D HMBC spectrum of **PGC8**

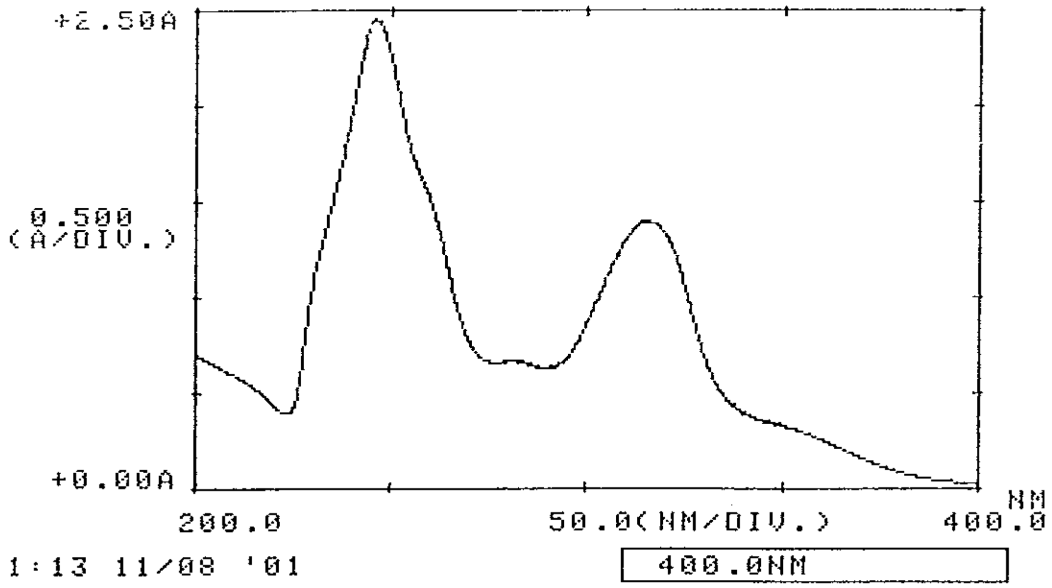


Figure 58 UV (EtOH) spectrum of **PGC9**

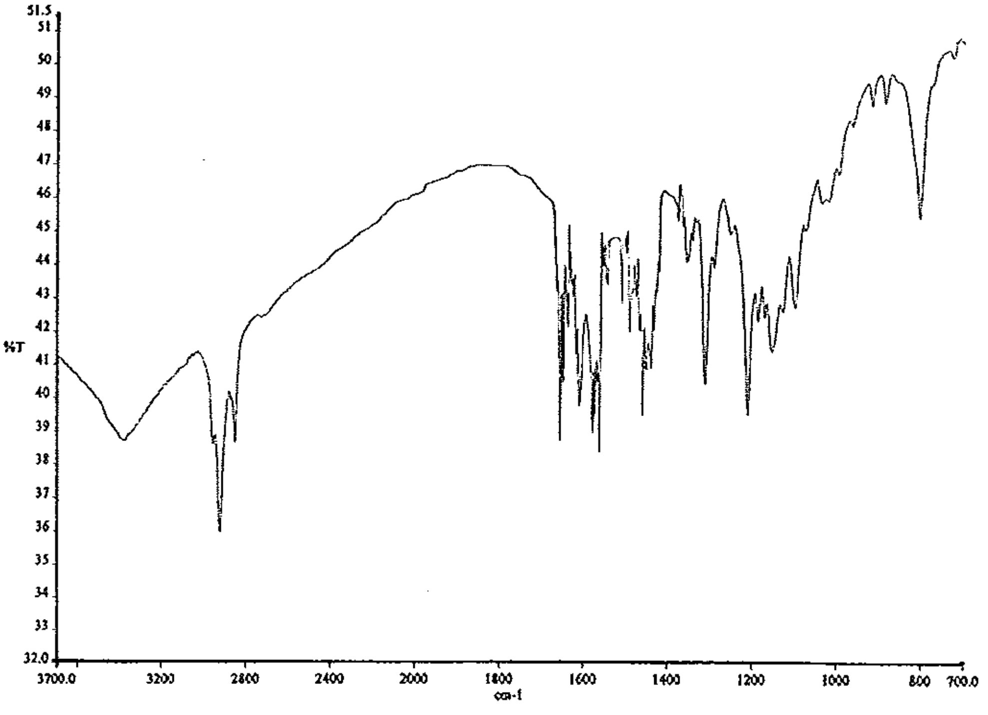


Figure 59 FT-IR (KBr) spectrum of **PGC9**

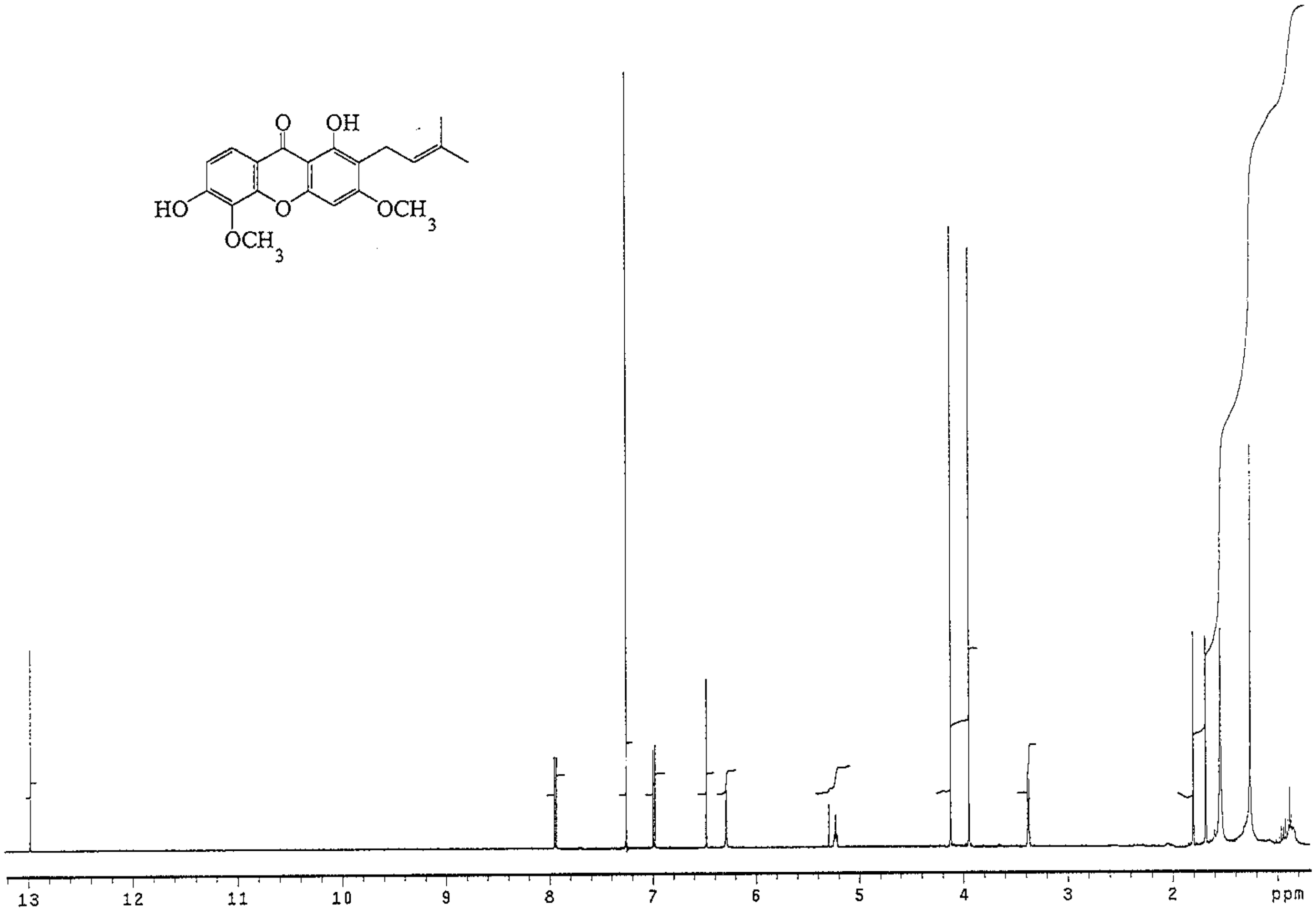


Figure 60 ^{1}H NMR (500 MHz)($CDCl_3$) spectrum of **PGC9**

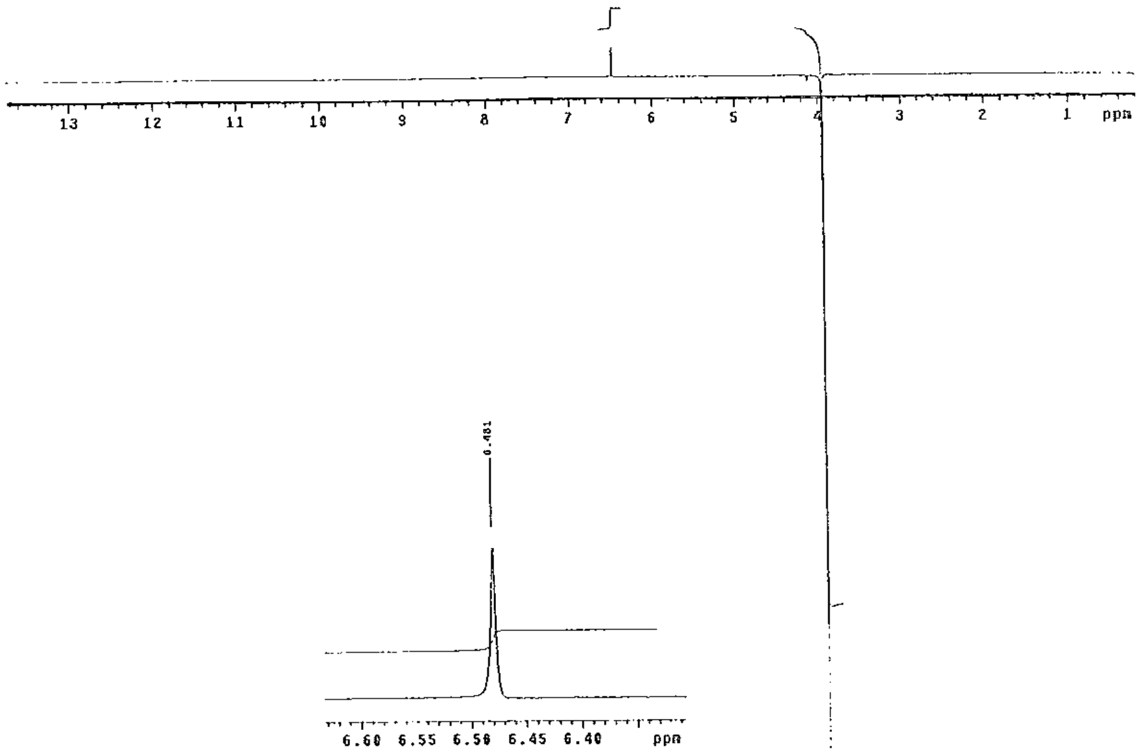


Figure 61 NOEDIFF spectrum of **PGC9** after irradiation at δ_H 3.95

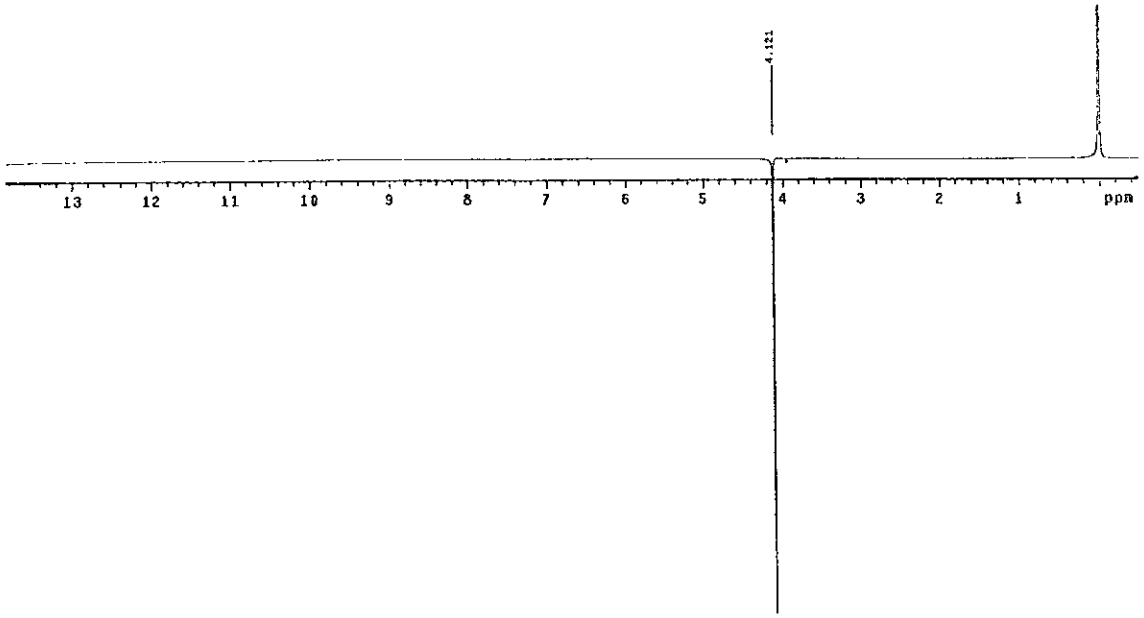


Figure 62 NOEDIFF spectrum of **PGC9** after irradiation at δ_H 4.12

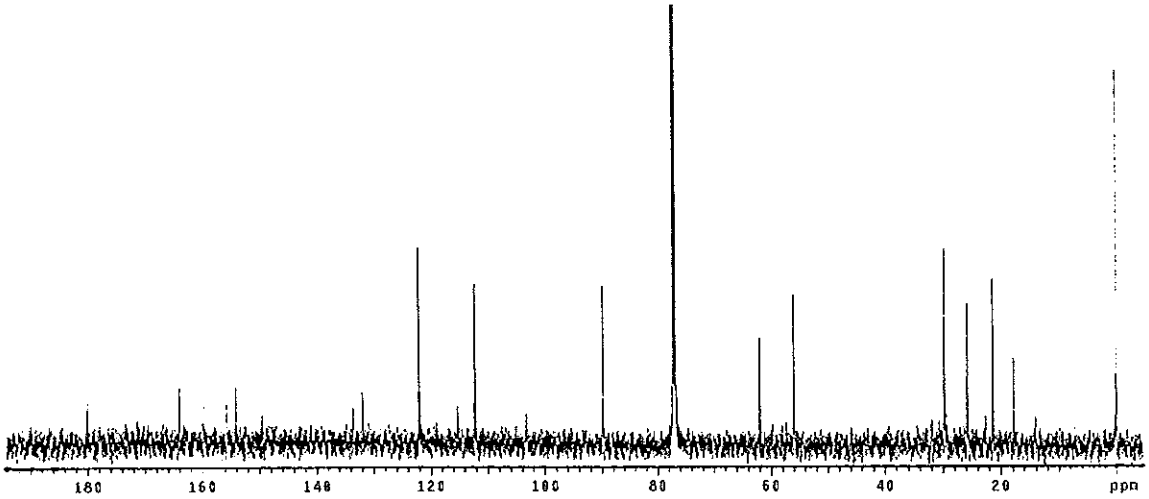


Figure 63 ^{13}C NMR (125 MHz)(CDCl$_3$) spectrum of **PGC9**

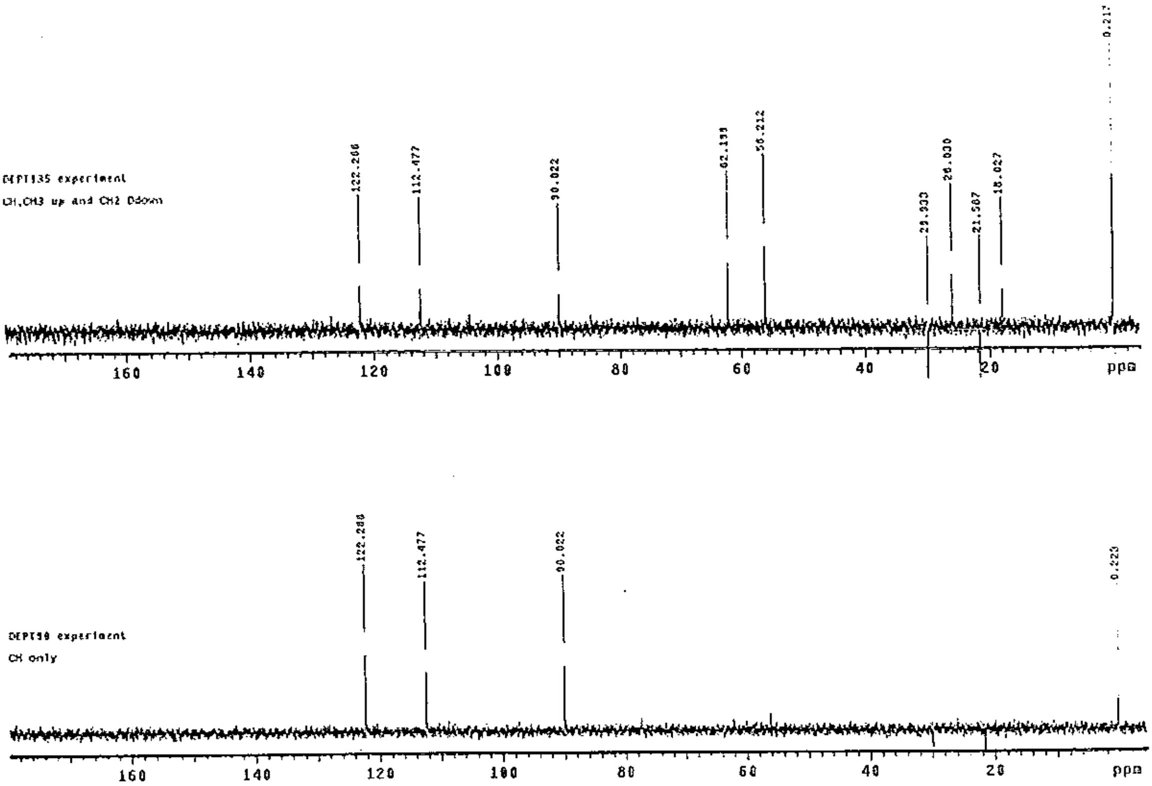


Figure 64 DEPT spectrum of **PGC9**

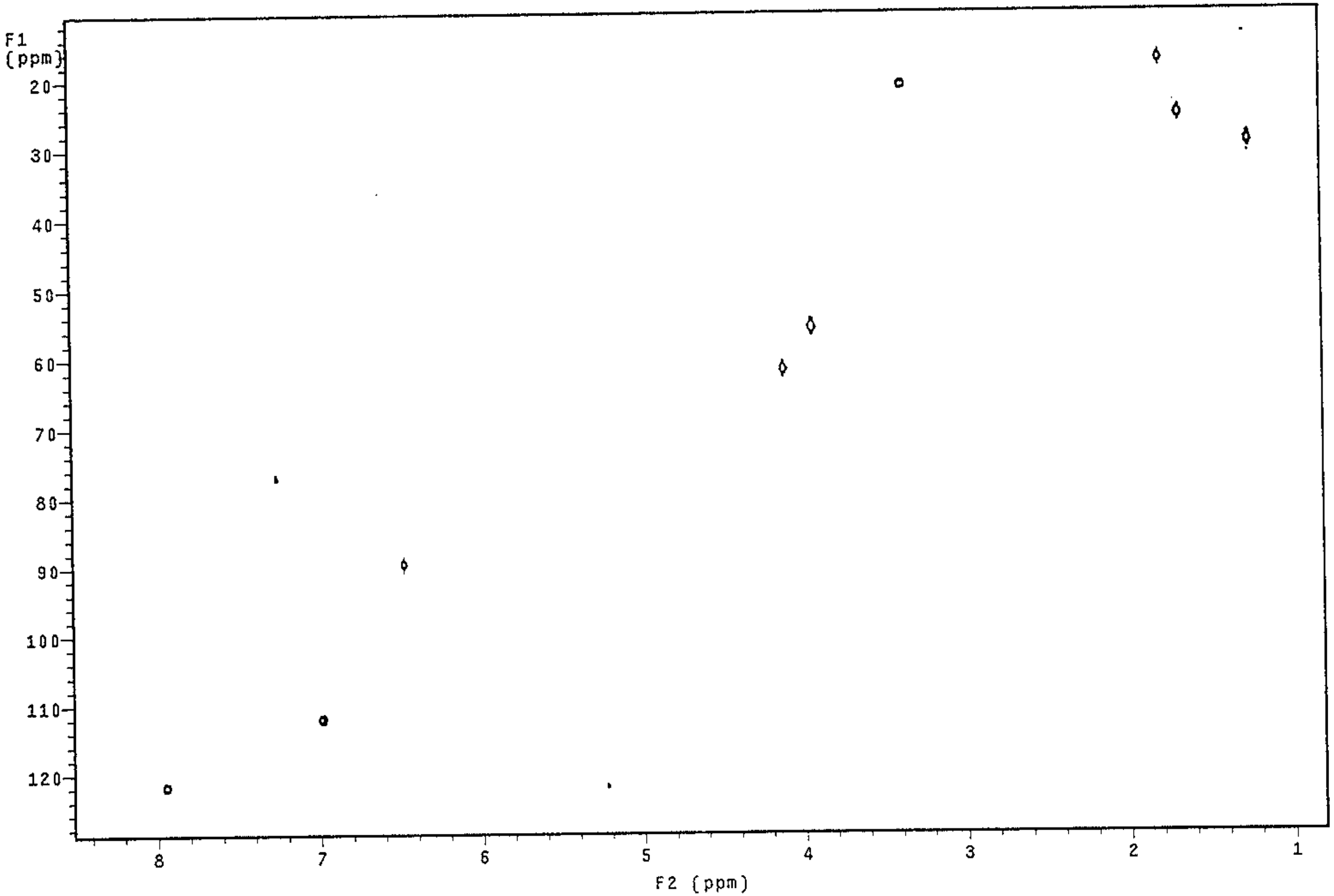


Figure 65 2D HMQC spectrum of **PGC9**

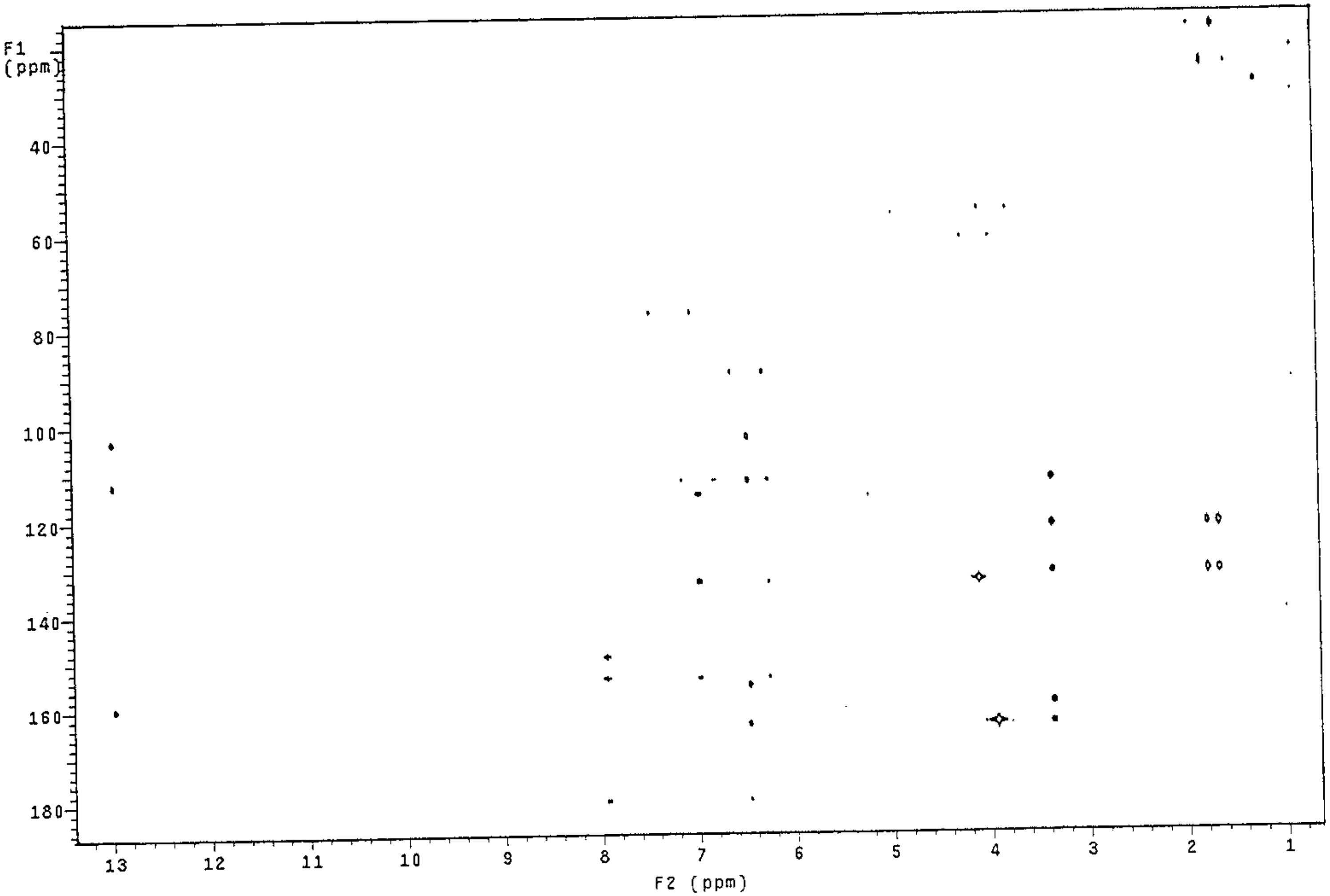


Figure 66 2D HMBC spectrum of **PGC9**

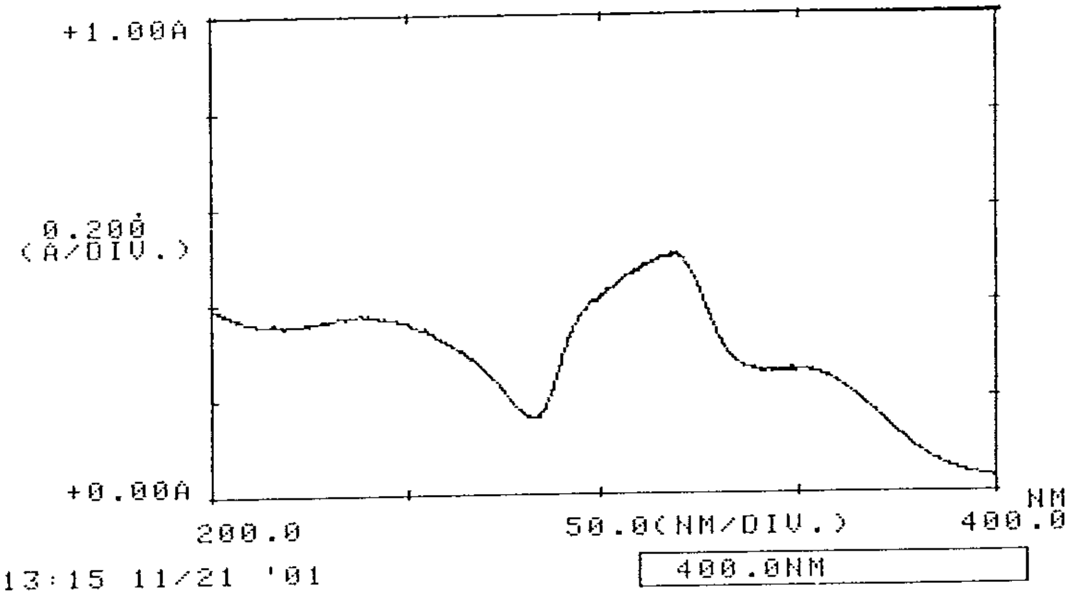


Figure 67 UV (EtOH) spectrum of **PGC10**

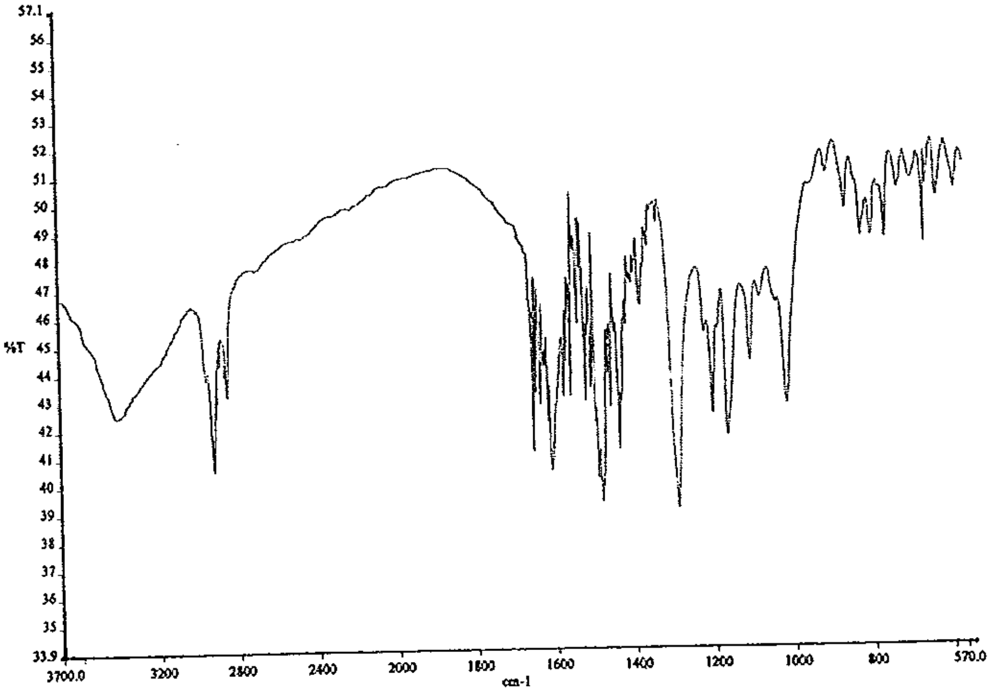


Figure 68 FT-IR (KBr) spectrum of **PGC10**

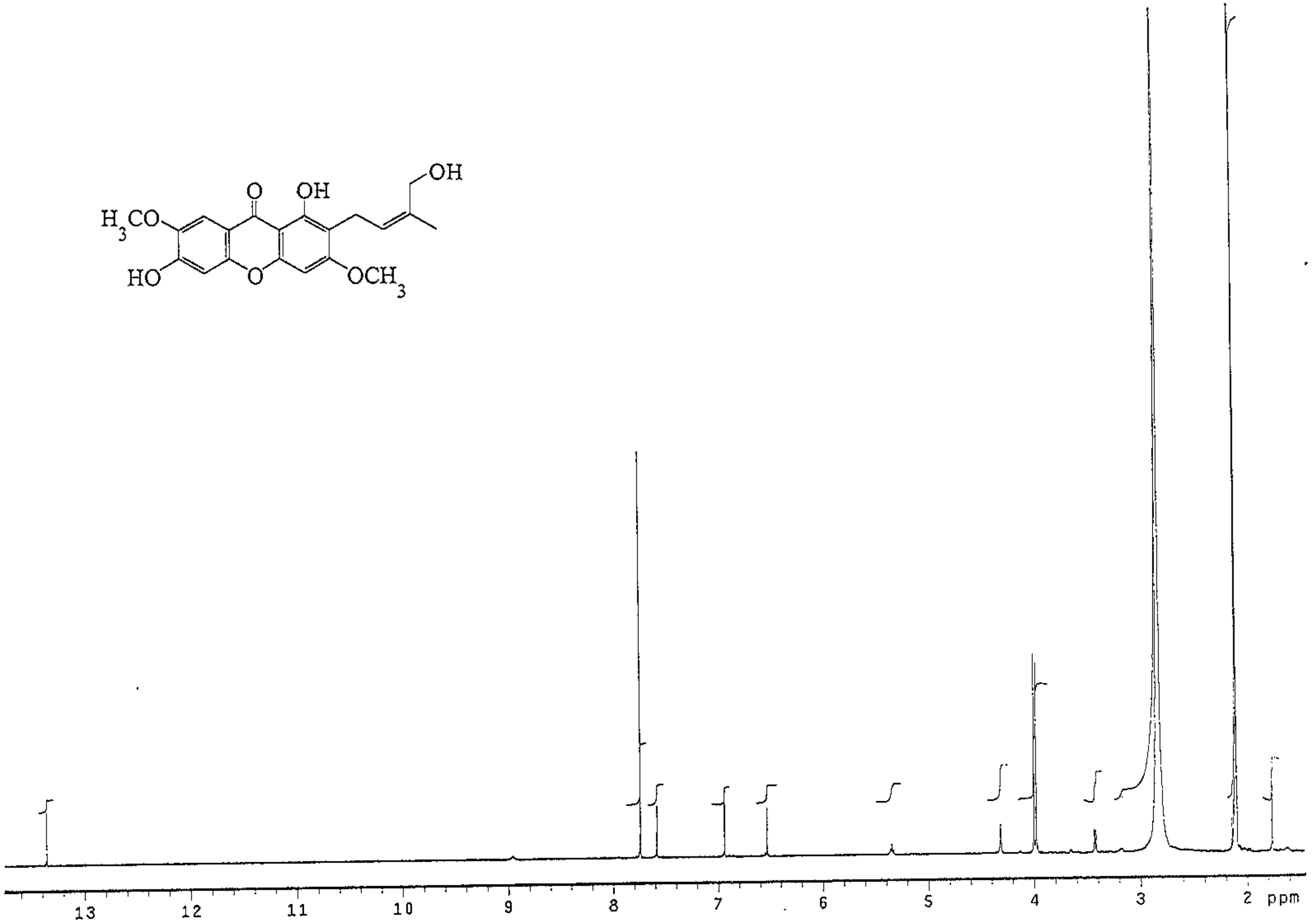


Figure 69 ^{1}H NMR (500 MHz)($CDCl_3$+CD_3COCD_3) spectrum of **PGC10**

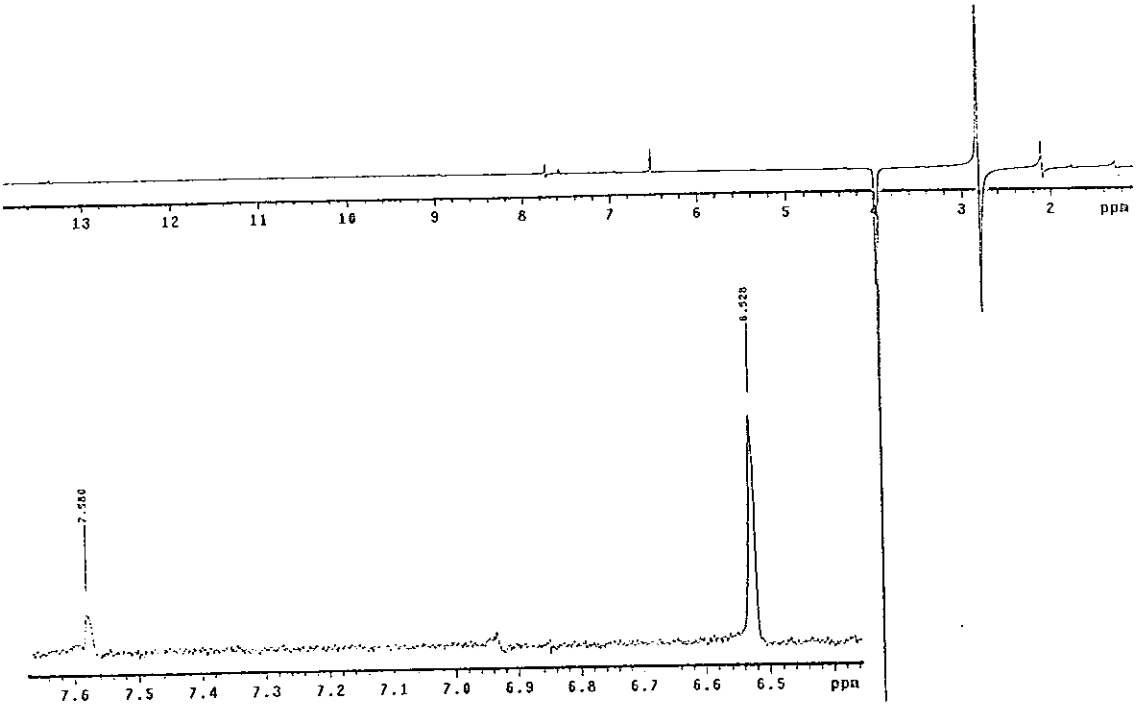


Figure 70 NOEDIFF spectrum of **PGC10** after irradiation at δ_H 3.98

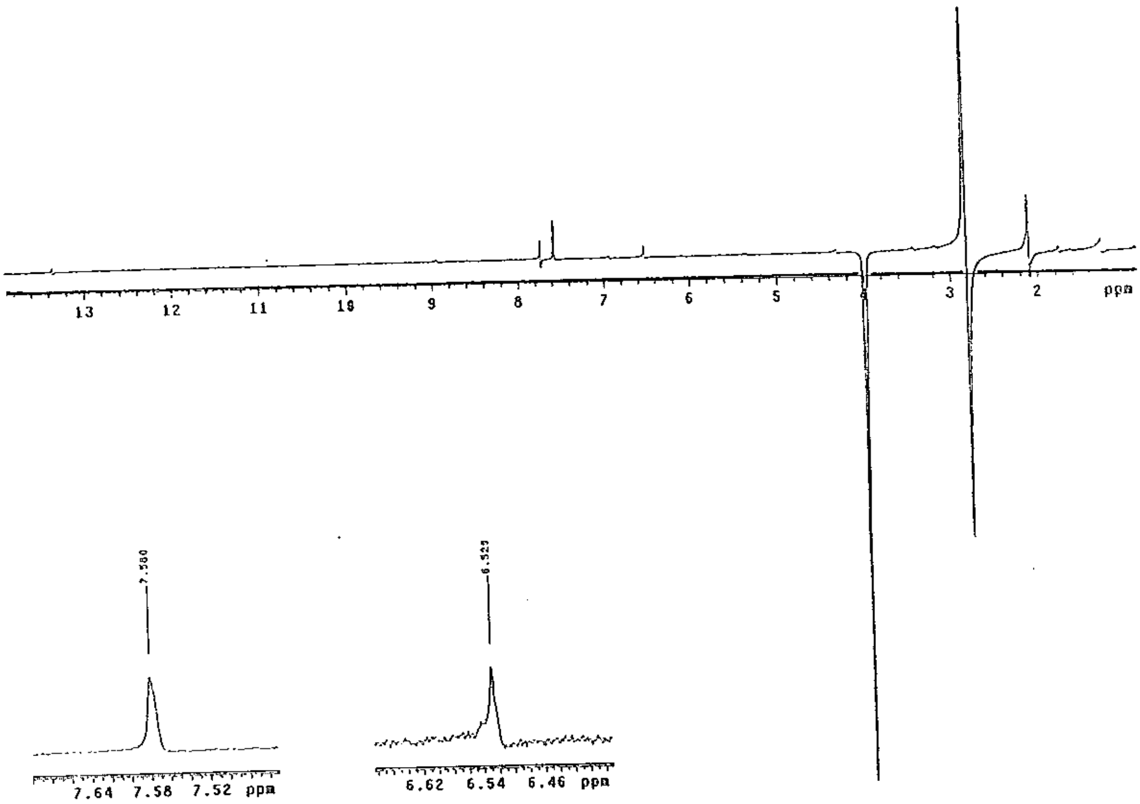


Figure 71 NOEDIFF spectrum of **PGC10** after irradiation at δ_H 4.00

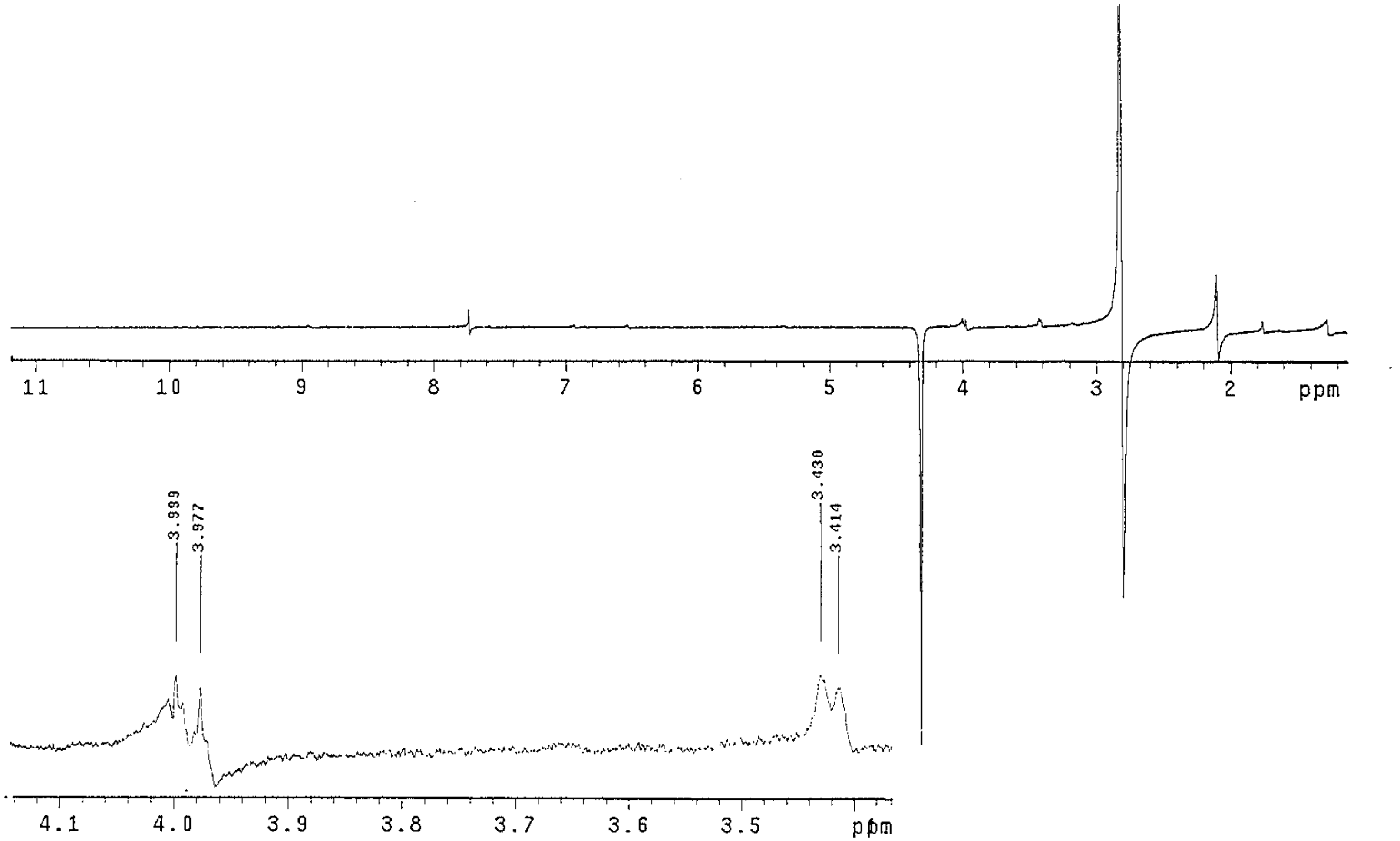


Figure 72 NOEDIFF spectrum of **PGC10** after irradiation at δ_H 4.32

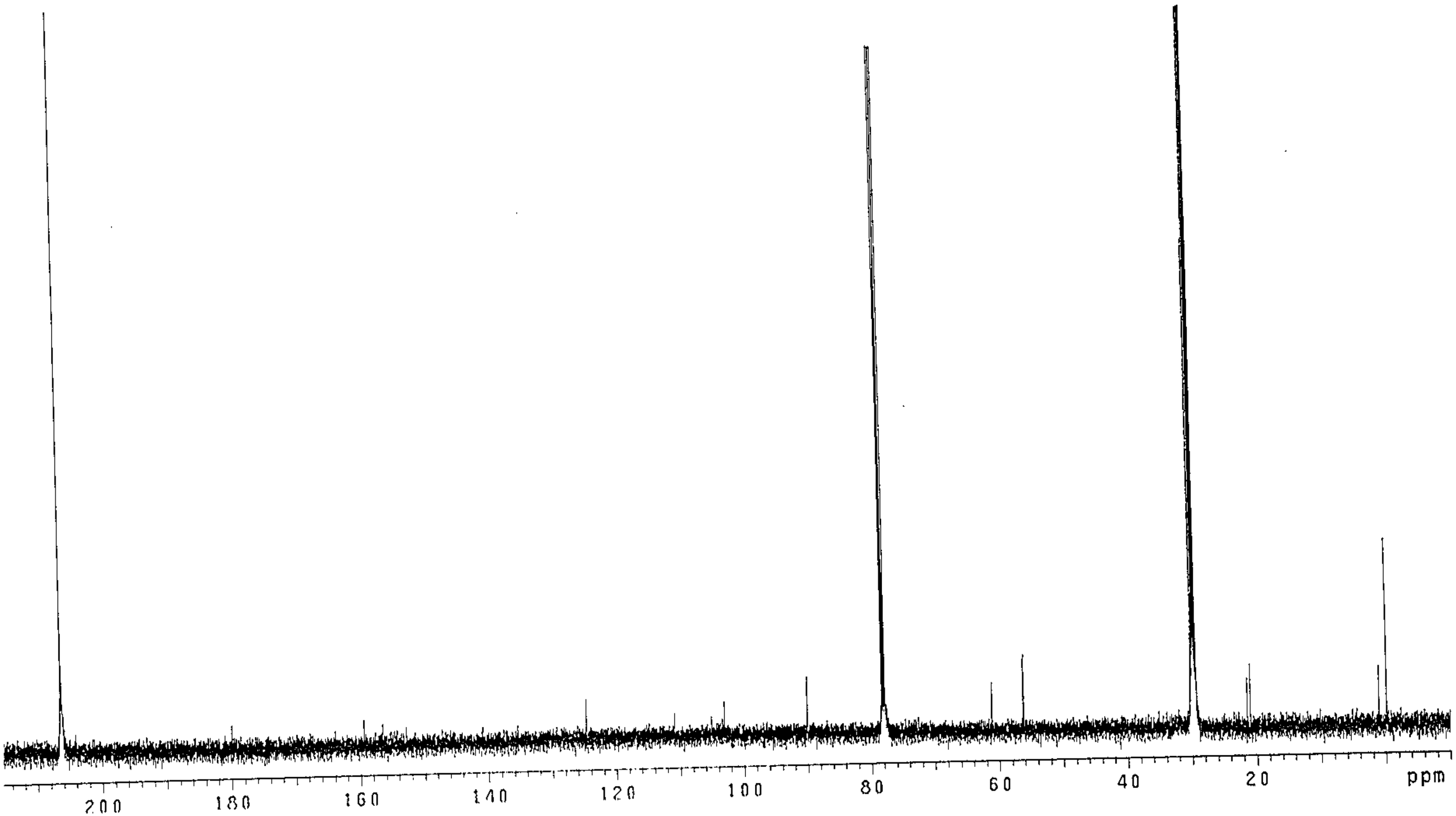


Figure 73 ^{13}C NMR (125 MHz)($CDCl_3$+CD_3COCD_3) spectrum of **PGC10**

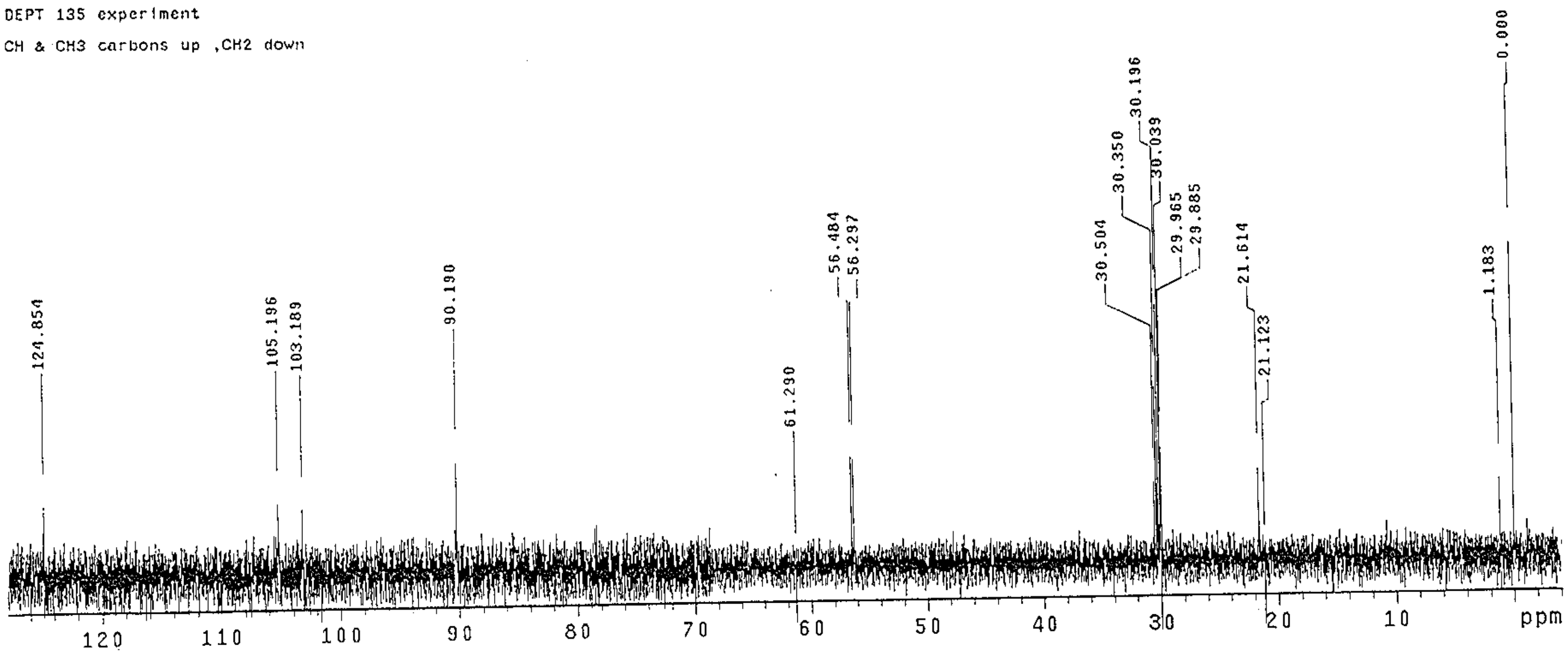


Figure 74 DEPT 135° spectrum of **PGC10**

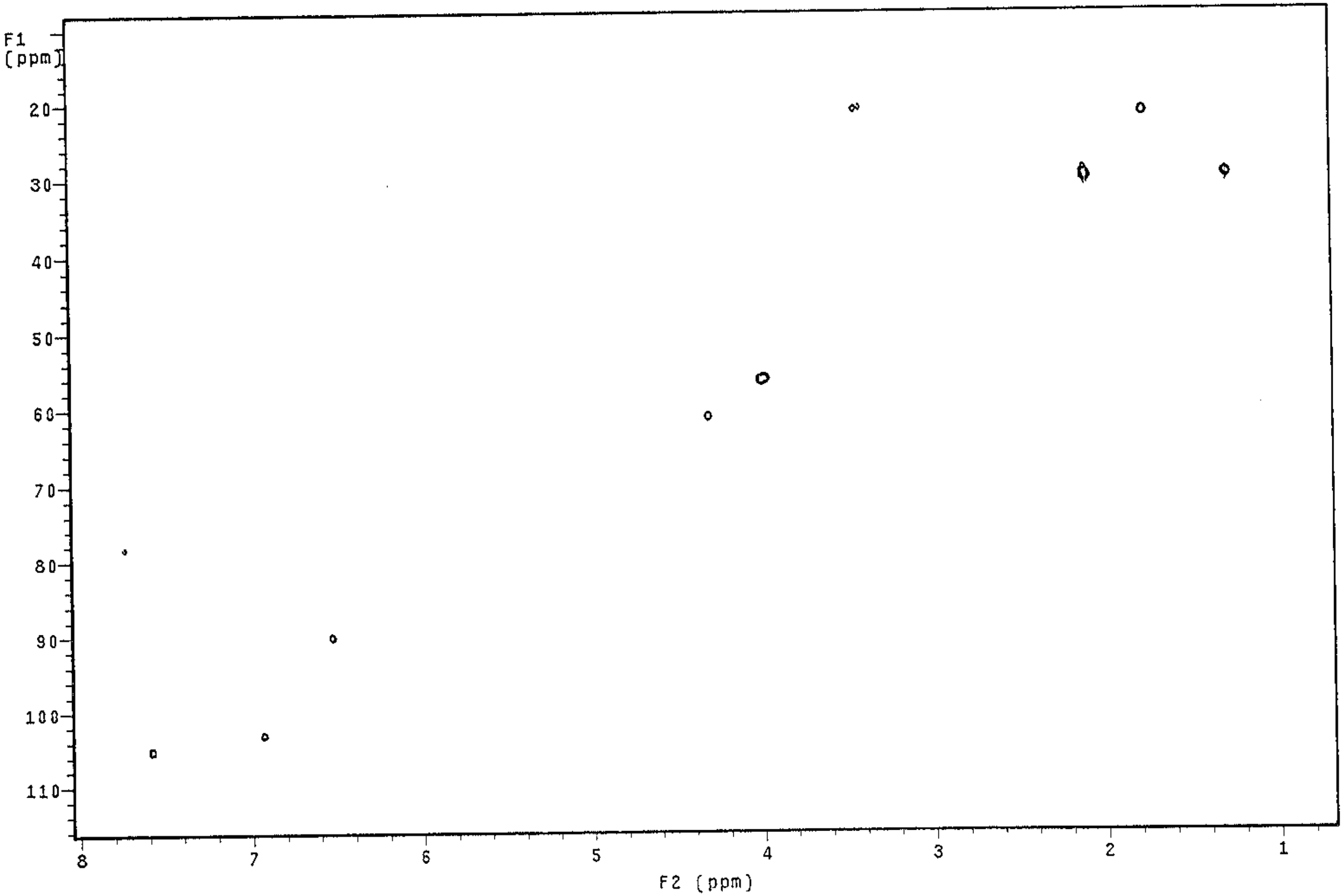


Figure 75 2D HMQC spectrum of **PGC10**

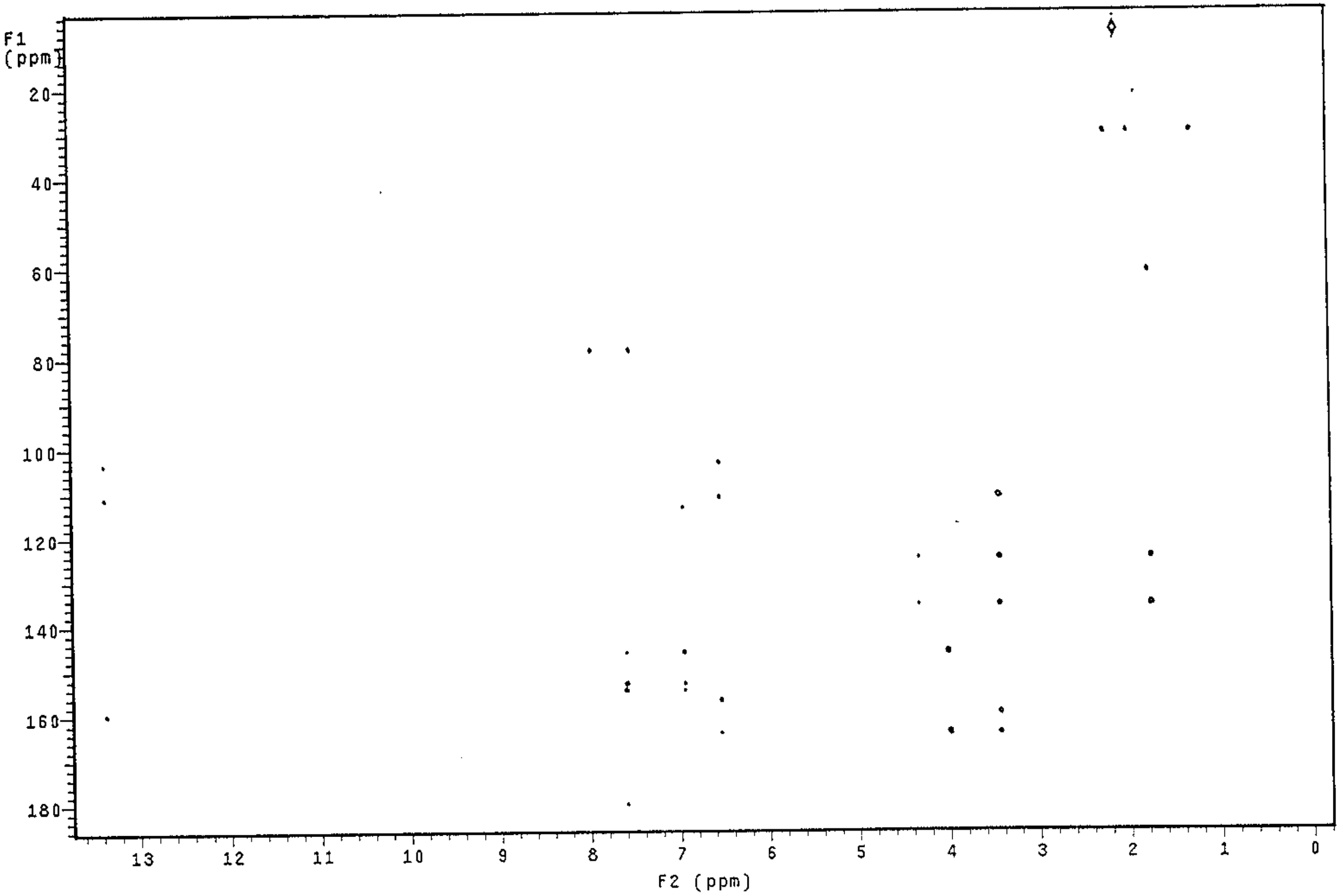


Figure 76 2D HMBC spectrum of **PGC10**

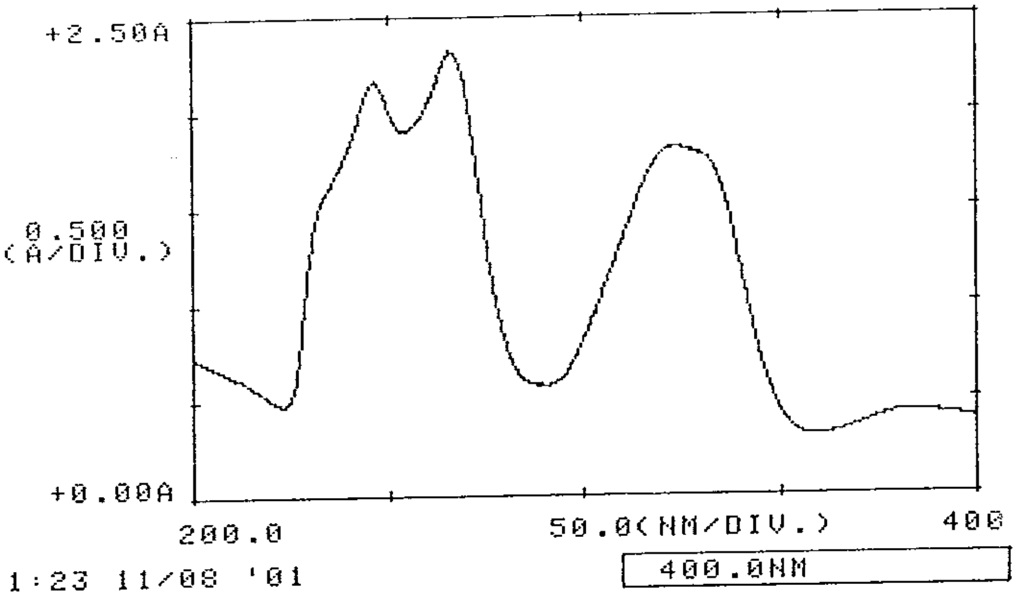


Figure 77 UV (EtOH) spectrum of **PGC11**

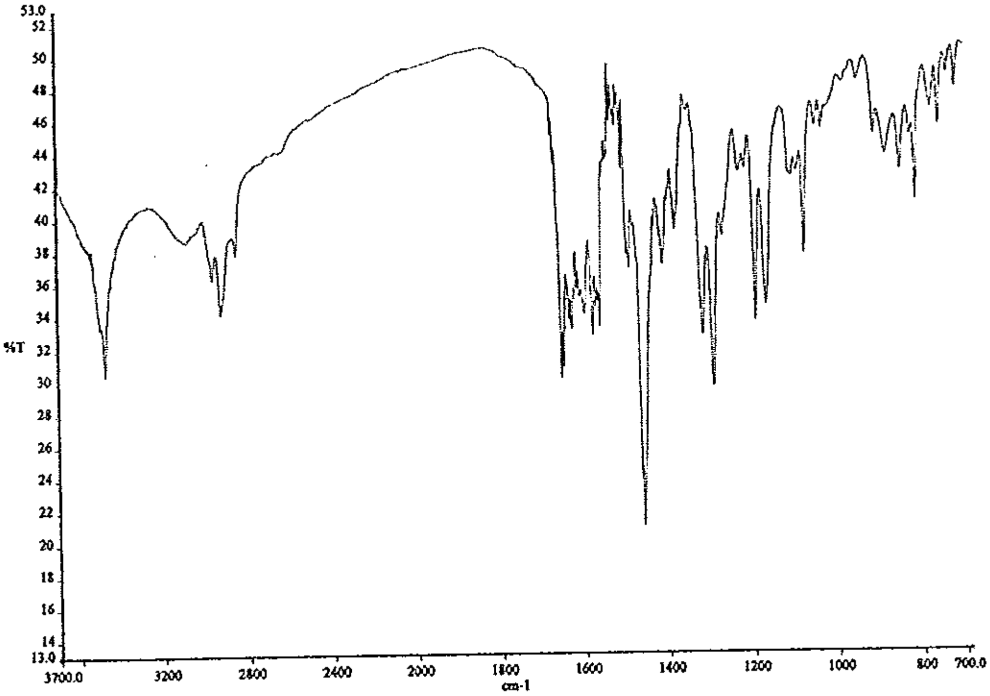


Figure 78 FT-IR (KBr) spectrum of **PGC11**

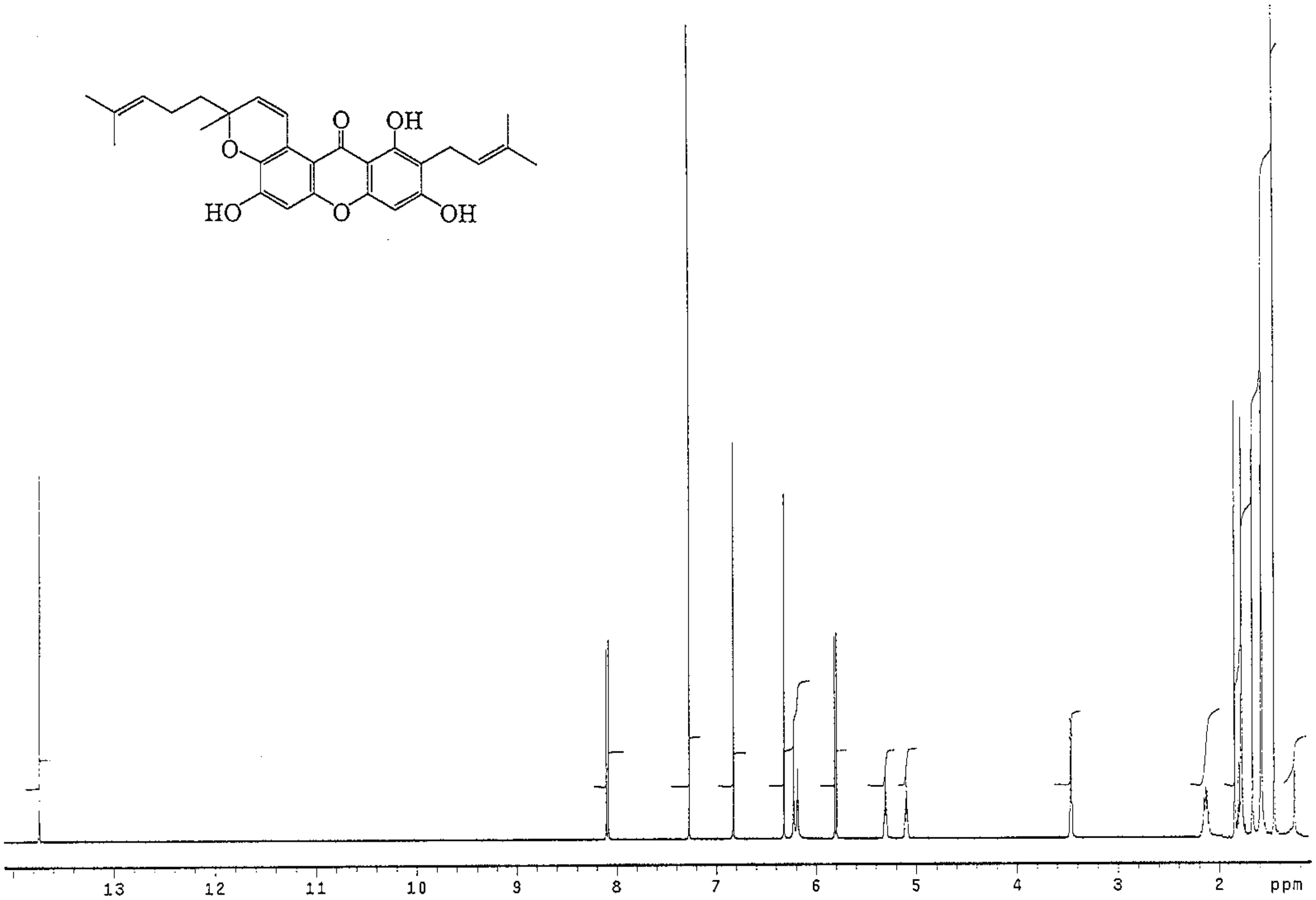


Figure 79 ^{1}H NMR (500 MHz)(CDCl$_3$) spectrum of **PGC11**

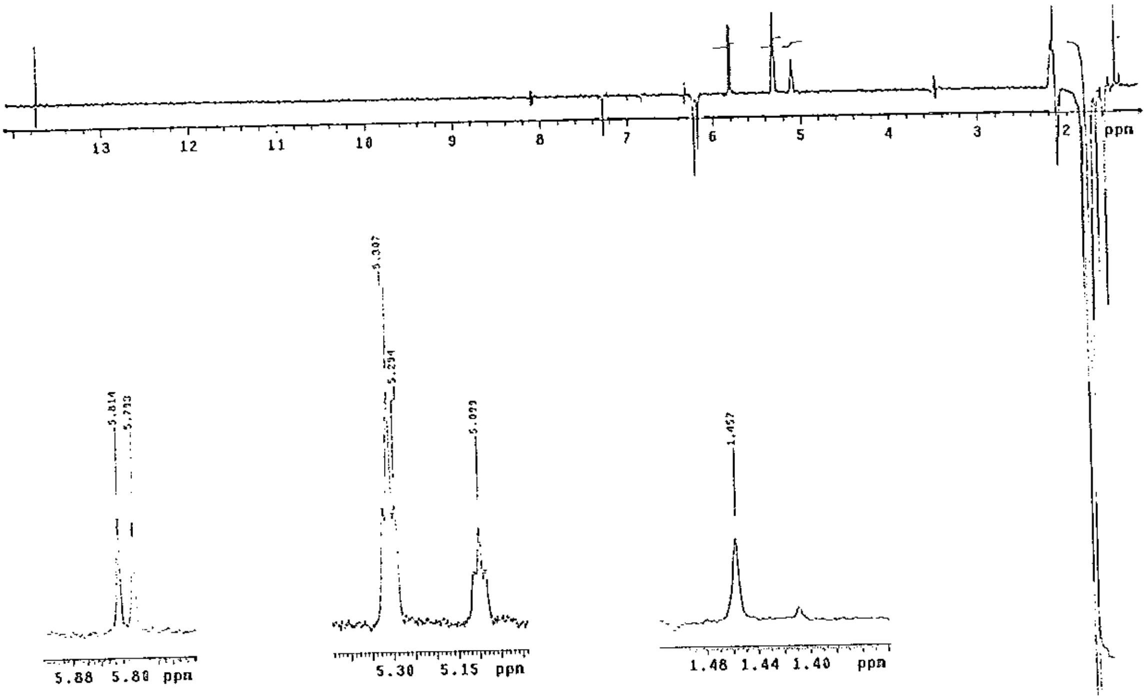


Figure 80 NOEDIFF spectrum of **PGC11** after irradiation at δ_H 1.78

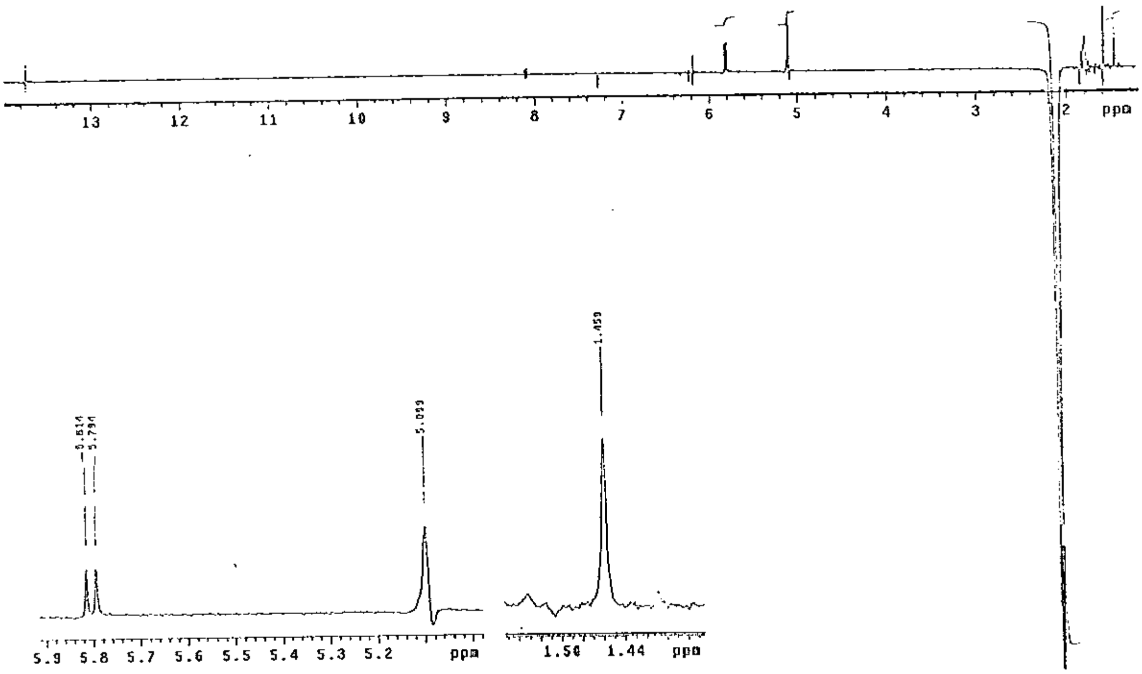


Figure 81 NOEDIFF spectrum of **PGC11** after irradiation at δ_H 2.14

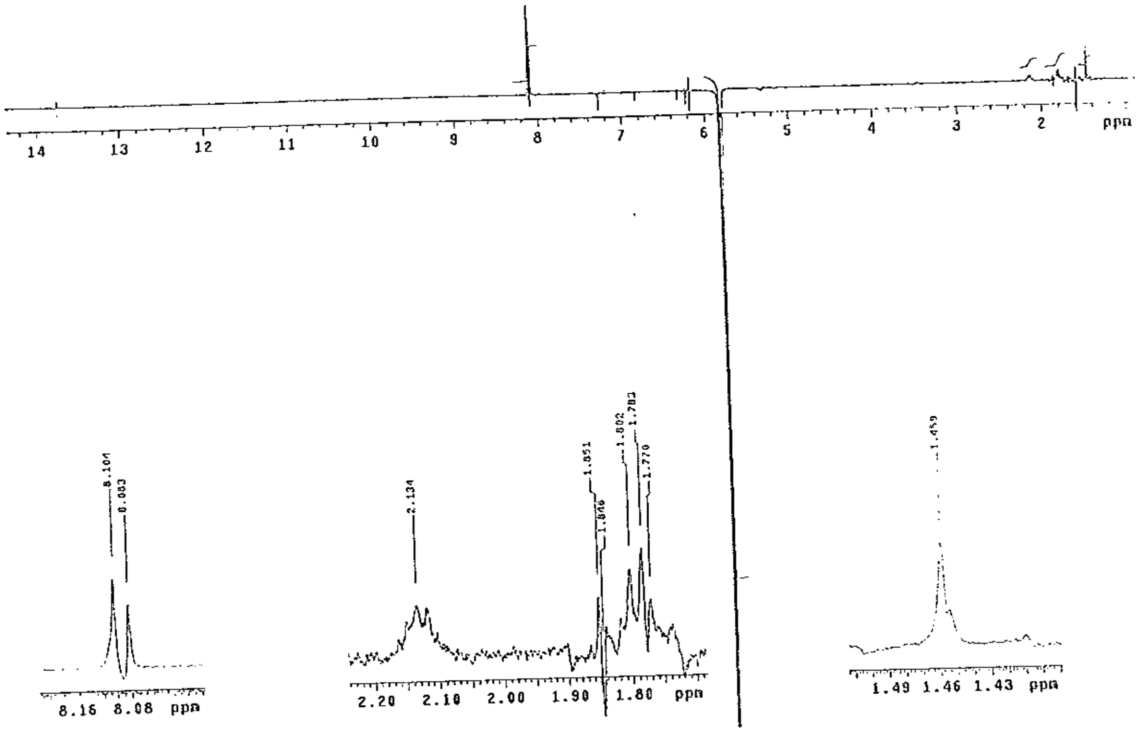


Figure 82 NOEDIFF spectrum of **PGC11** after irradiation at δ_H 5.81

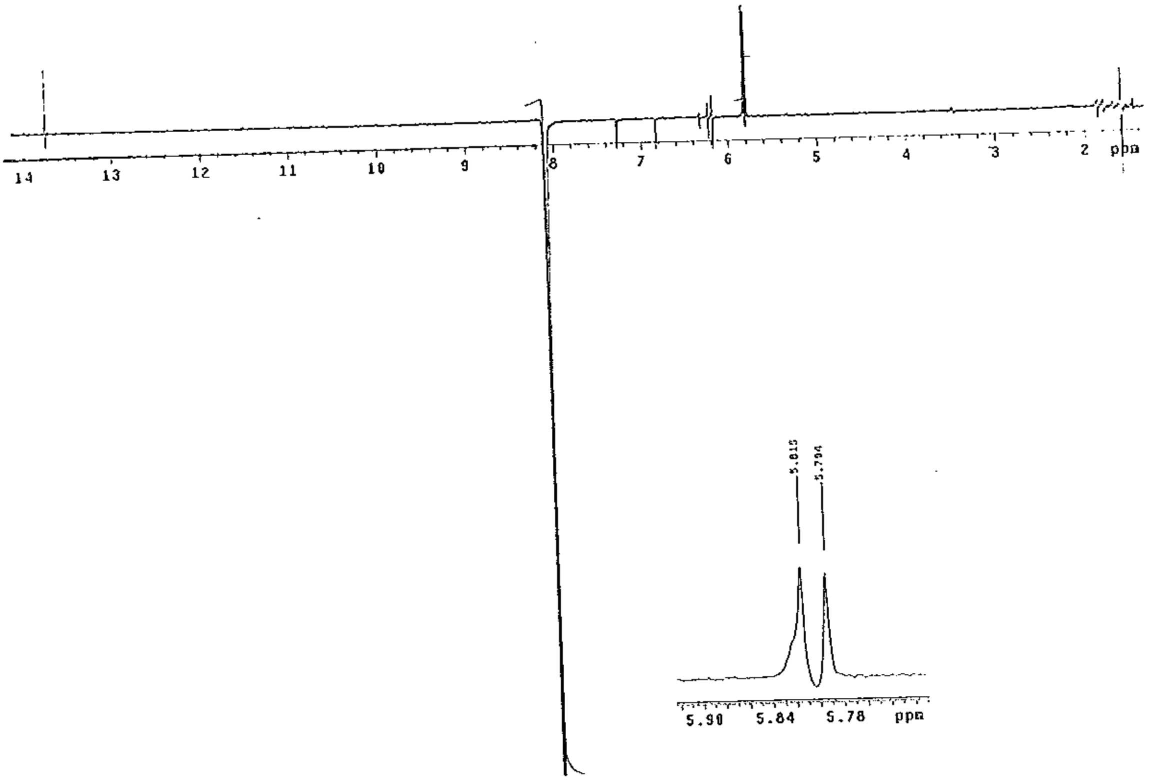


Figure 83 NOEDIFF spectrum of **PGC11** after irradiation at δ_H 8.09

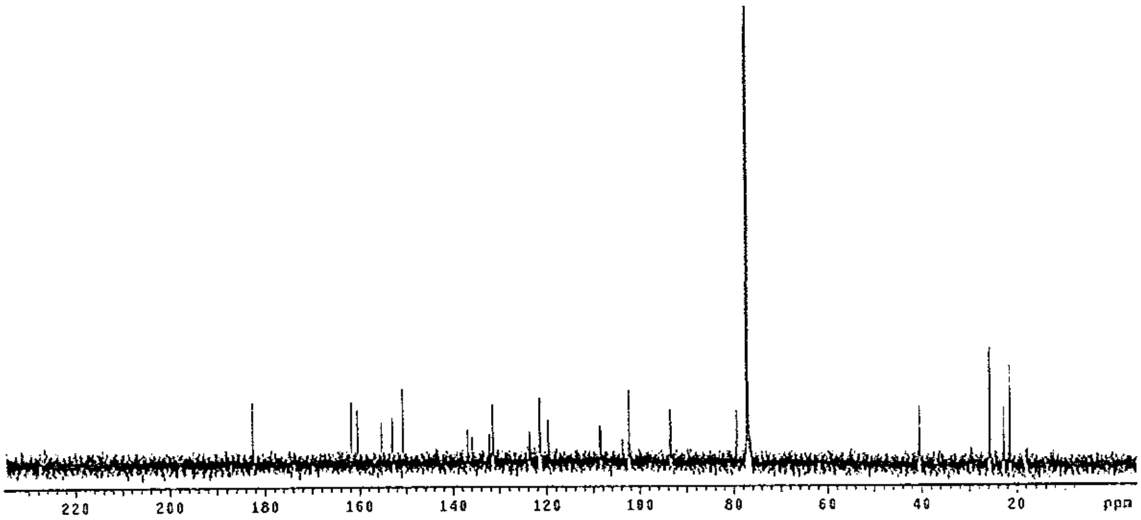


Figure 84 ^{13}C NMR (125 MHz)(CDCl$_3$) spectrum of **PGC11**

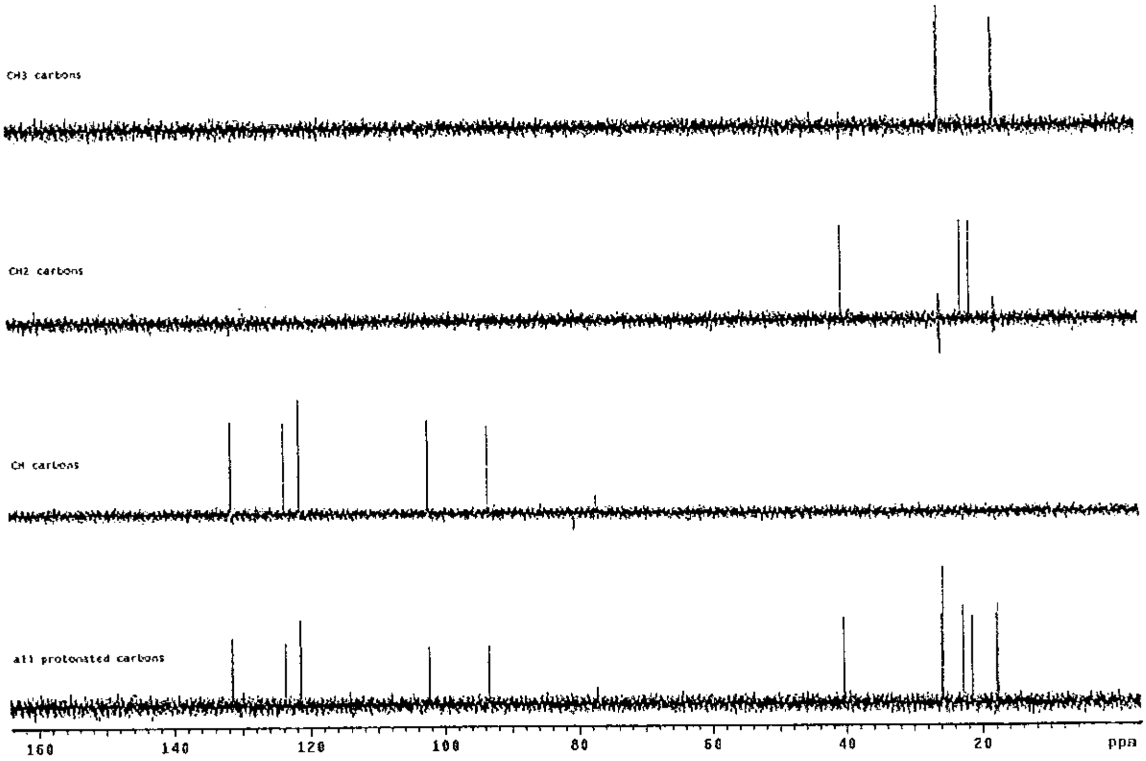


Figure 85 DEPT spectrum of **PGC11**

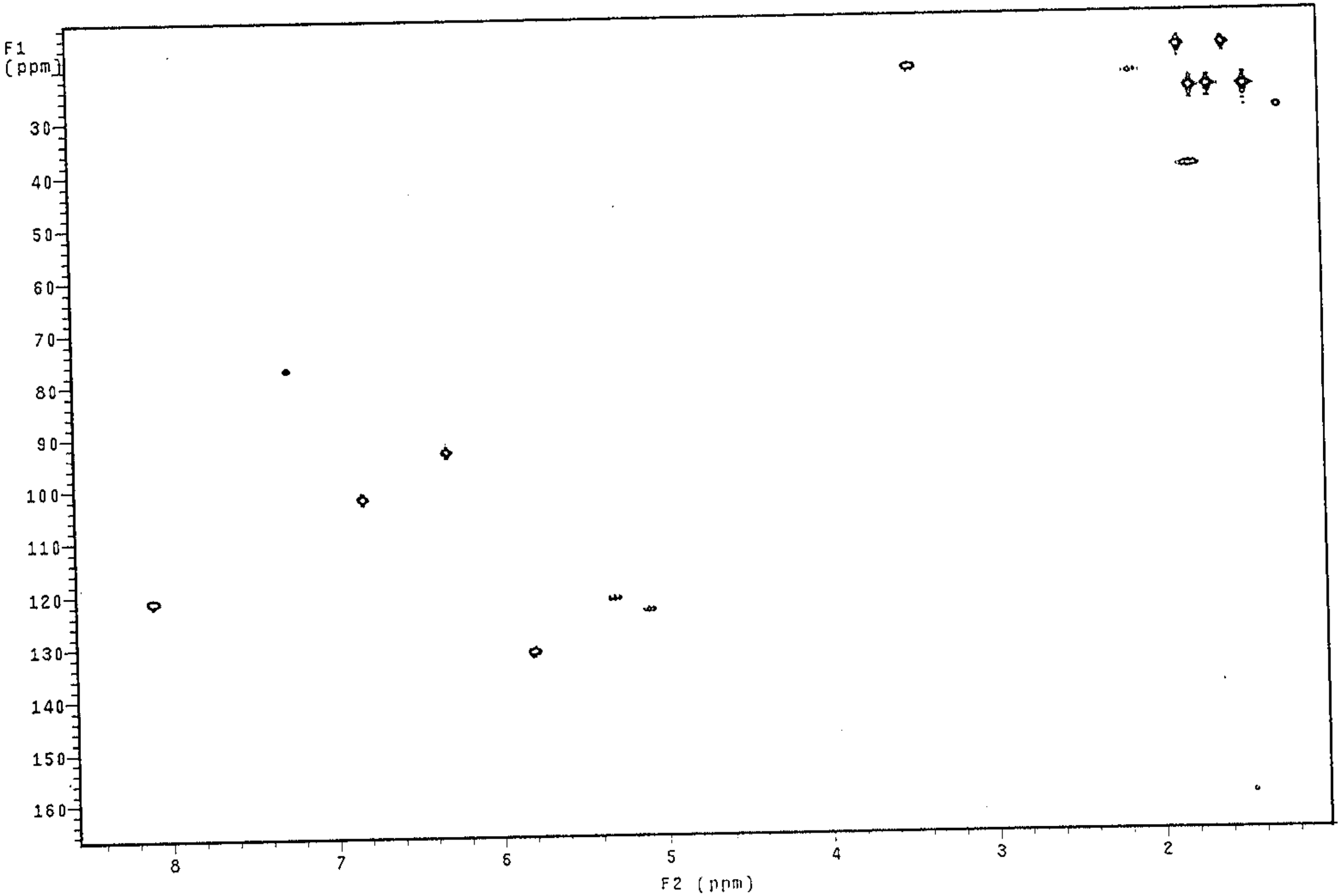


Figure 86 2D HMQC spectrum of **PGC11**

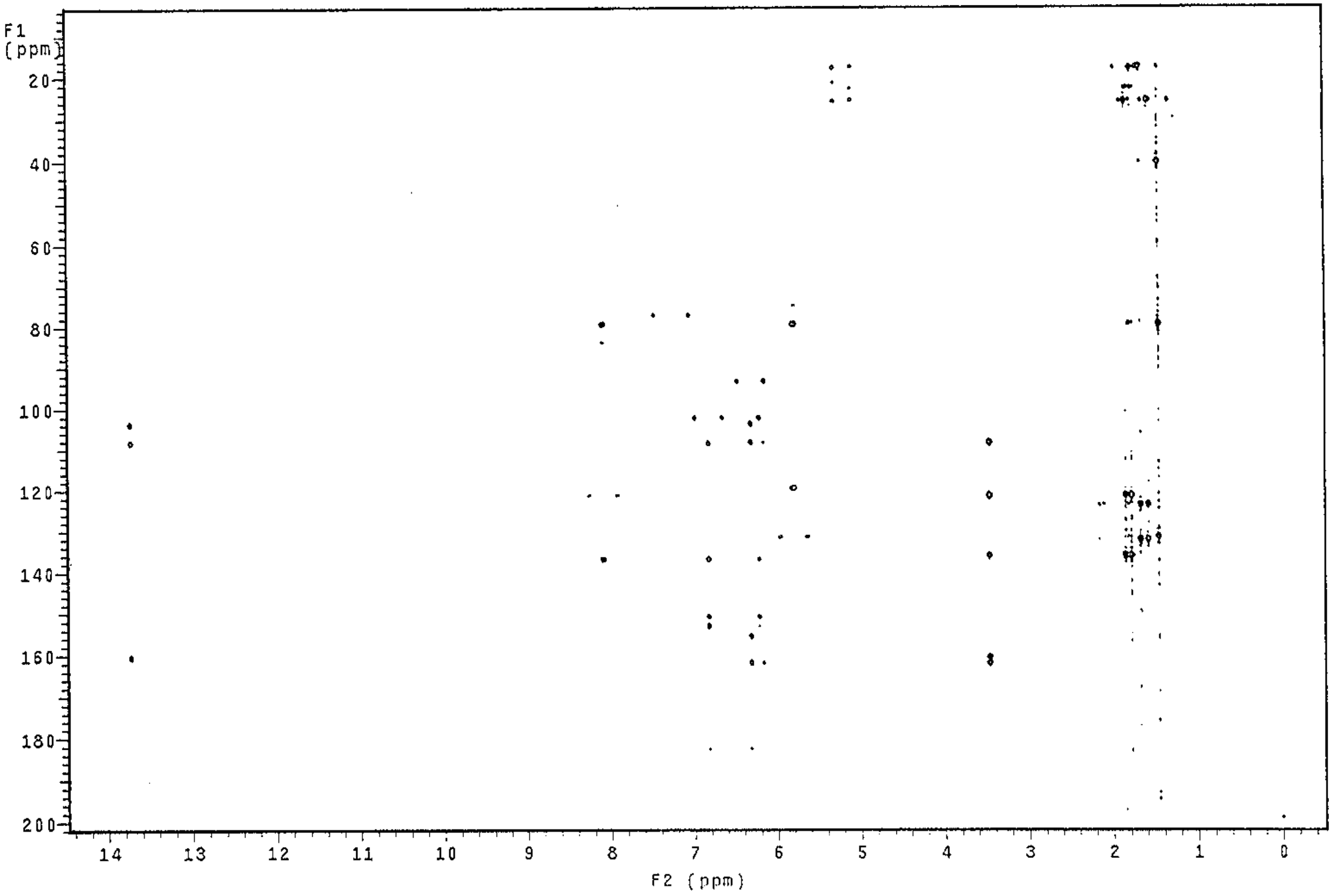


Figure 87 2D HMBC spectrum of **PGC11**

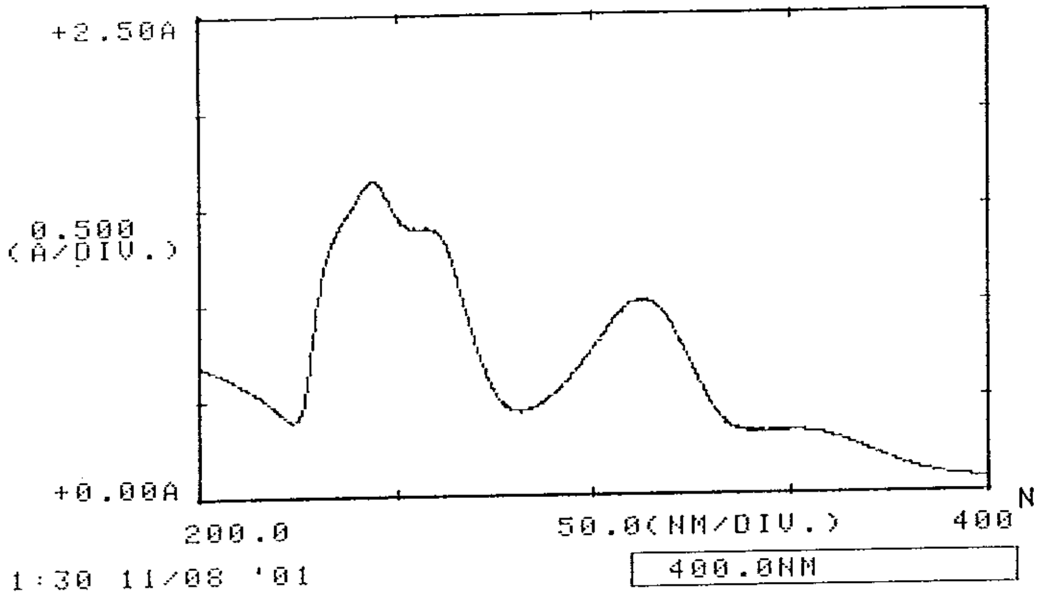


Figure 88 UV (EtOH) spectrum of **PGC12**

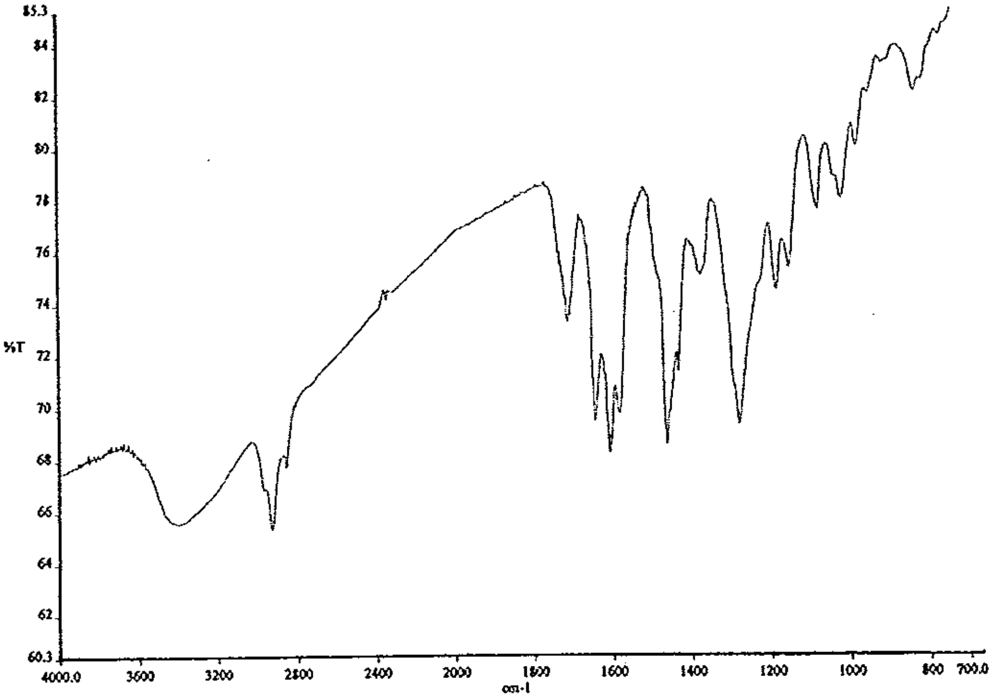


Figure 89 FT-IR (neat) spectrum of **PGC12**

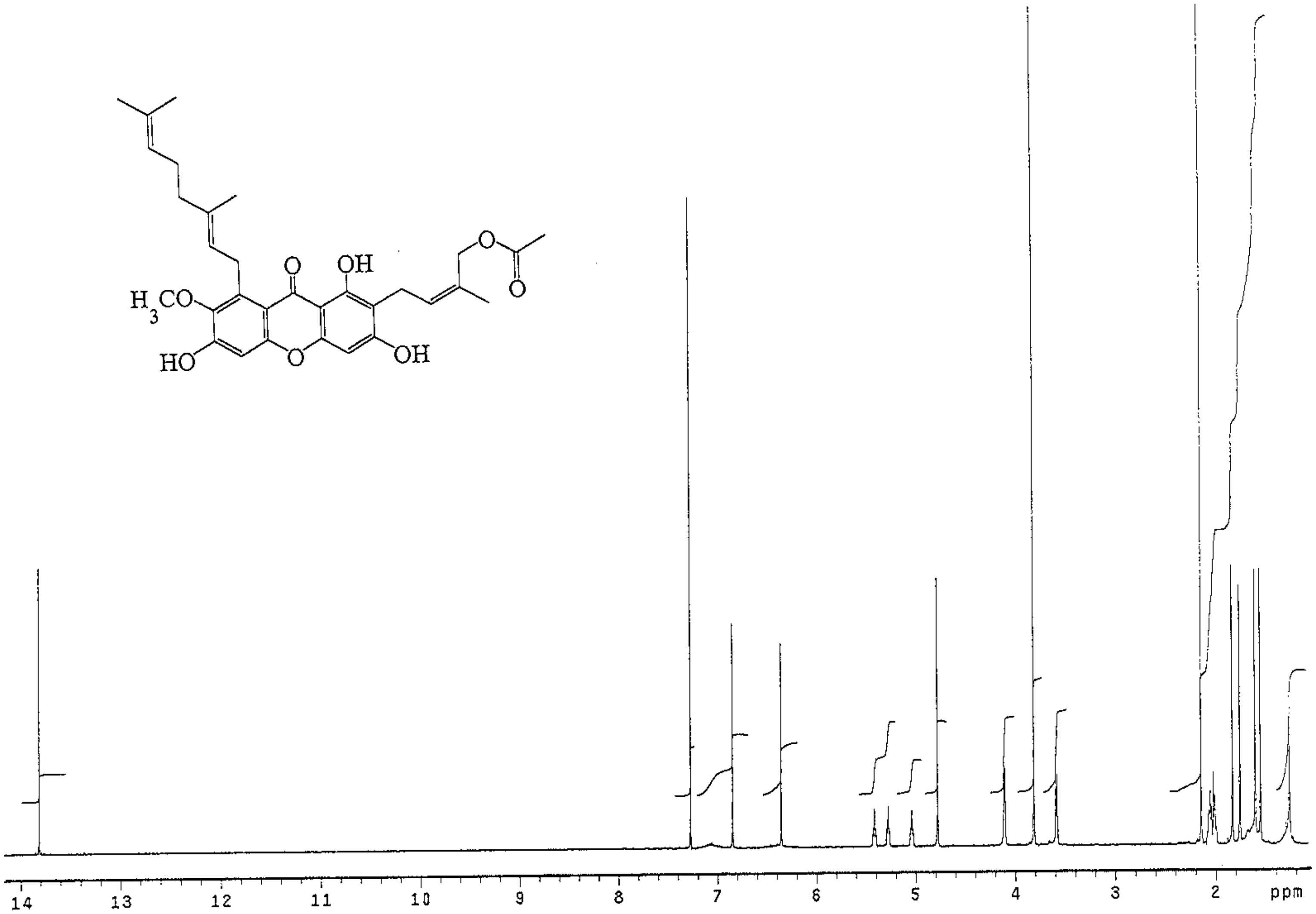


Figure 90 ^{1}H NMR (500 MHz)(CDCl$_3$) spectrum of **PGC12**

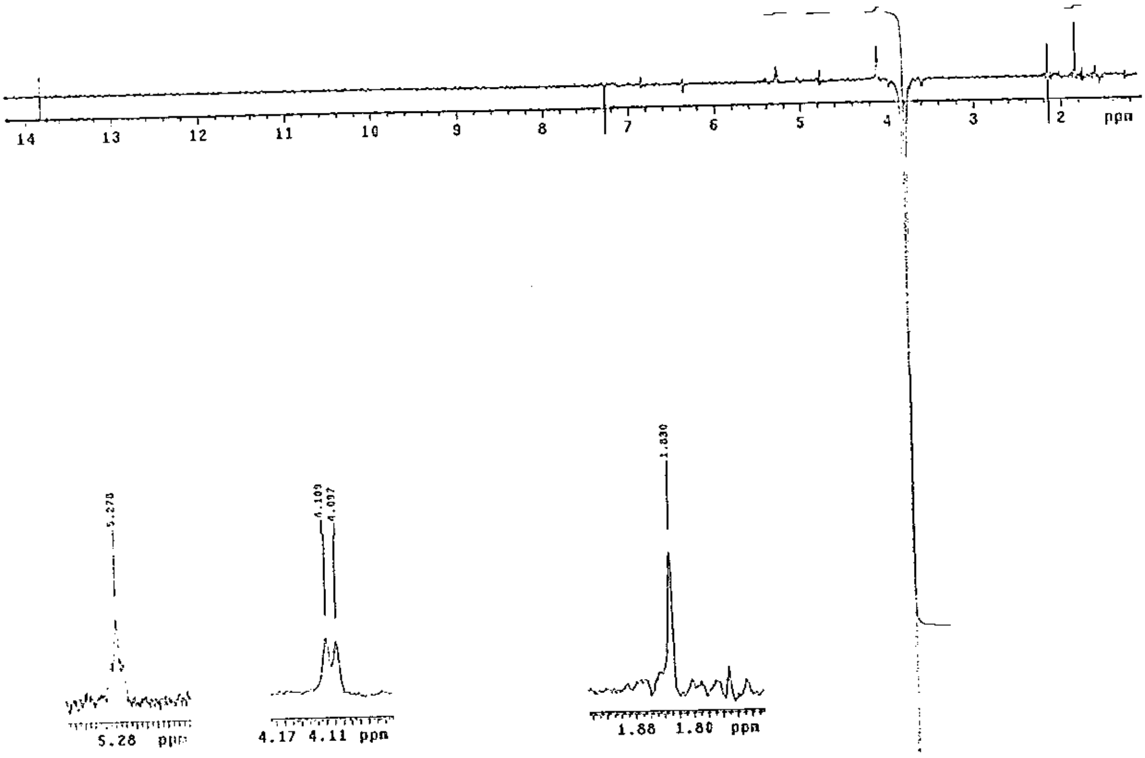


Figure 91 NOEDIFF spectrum of **PGC12** after irradiation at δ_H 3.81 ppm

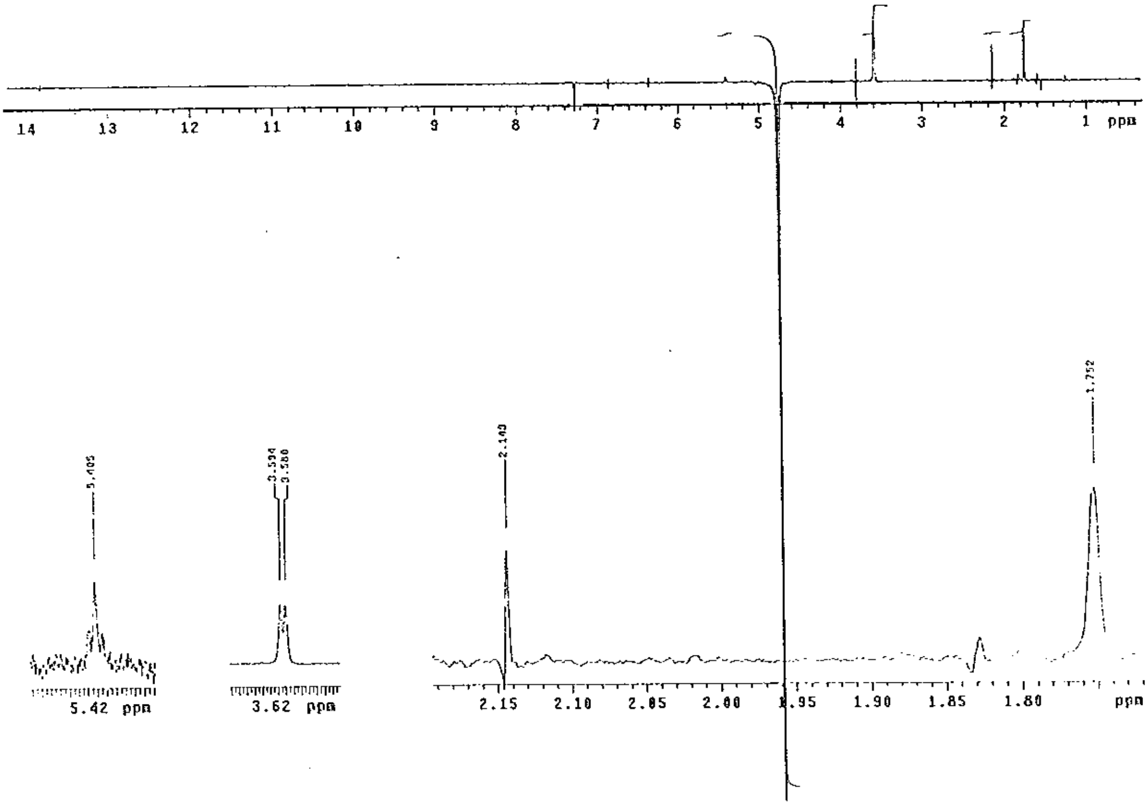


Figure 92 NOEDIFF spectrum of **PGC12** after irradiation at δ_H 4.77 ppm

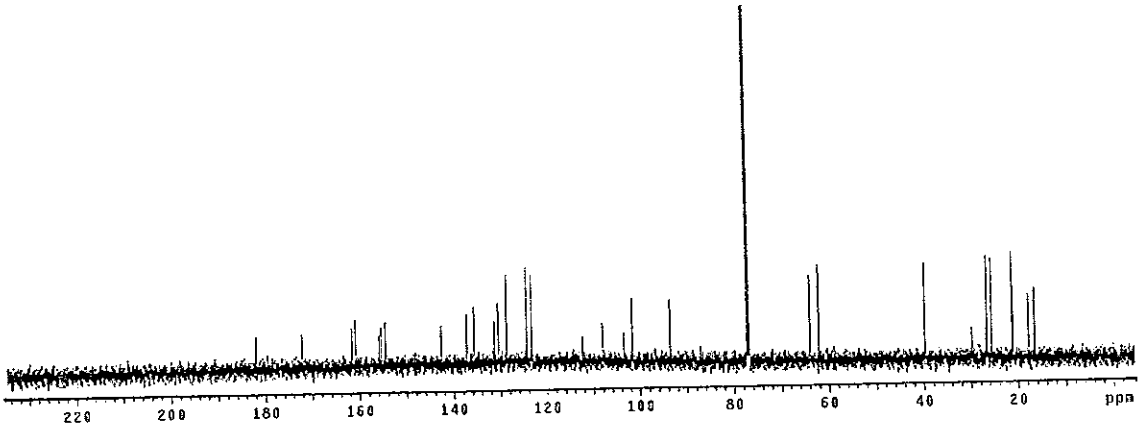


Figure 93 ^{13}C NMR (125 MHz)(CDCl$_3$) spectrum of **PGC12**

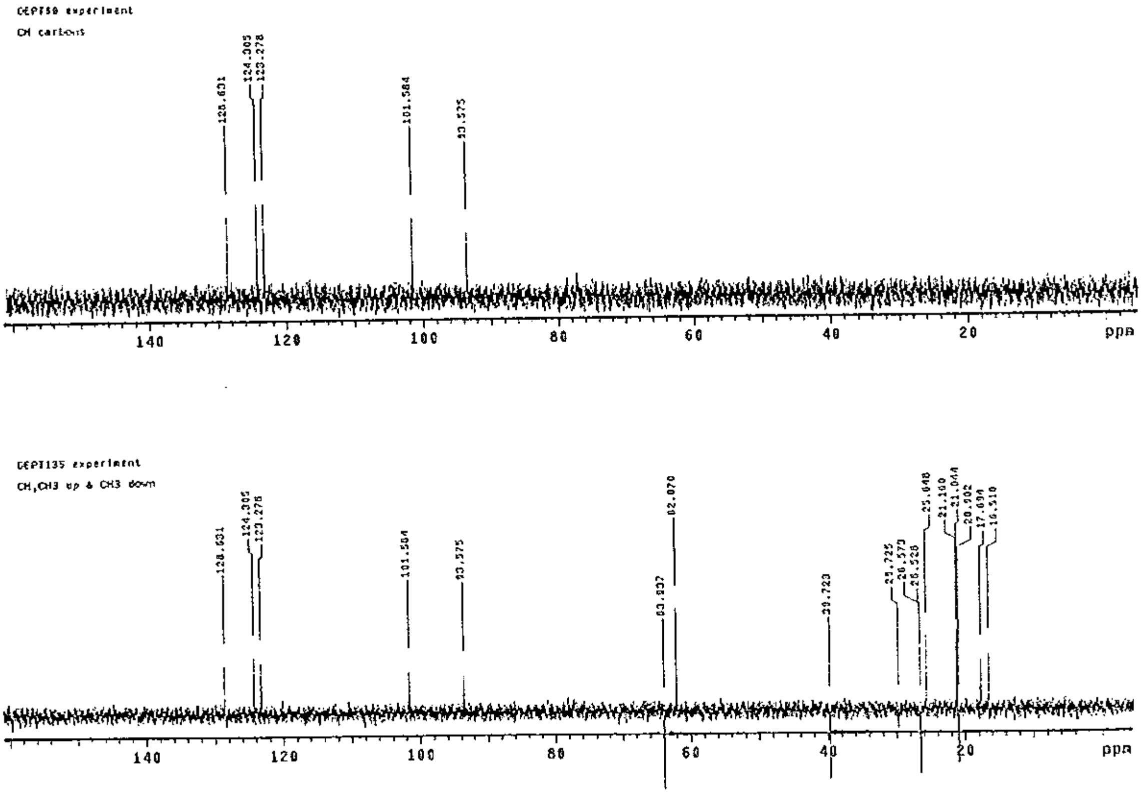


Figure 94 DEPT spectrum of **PGC12**

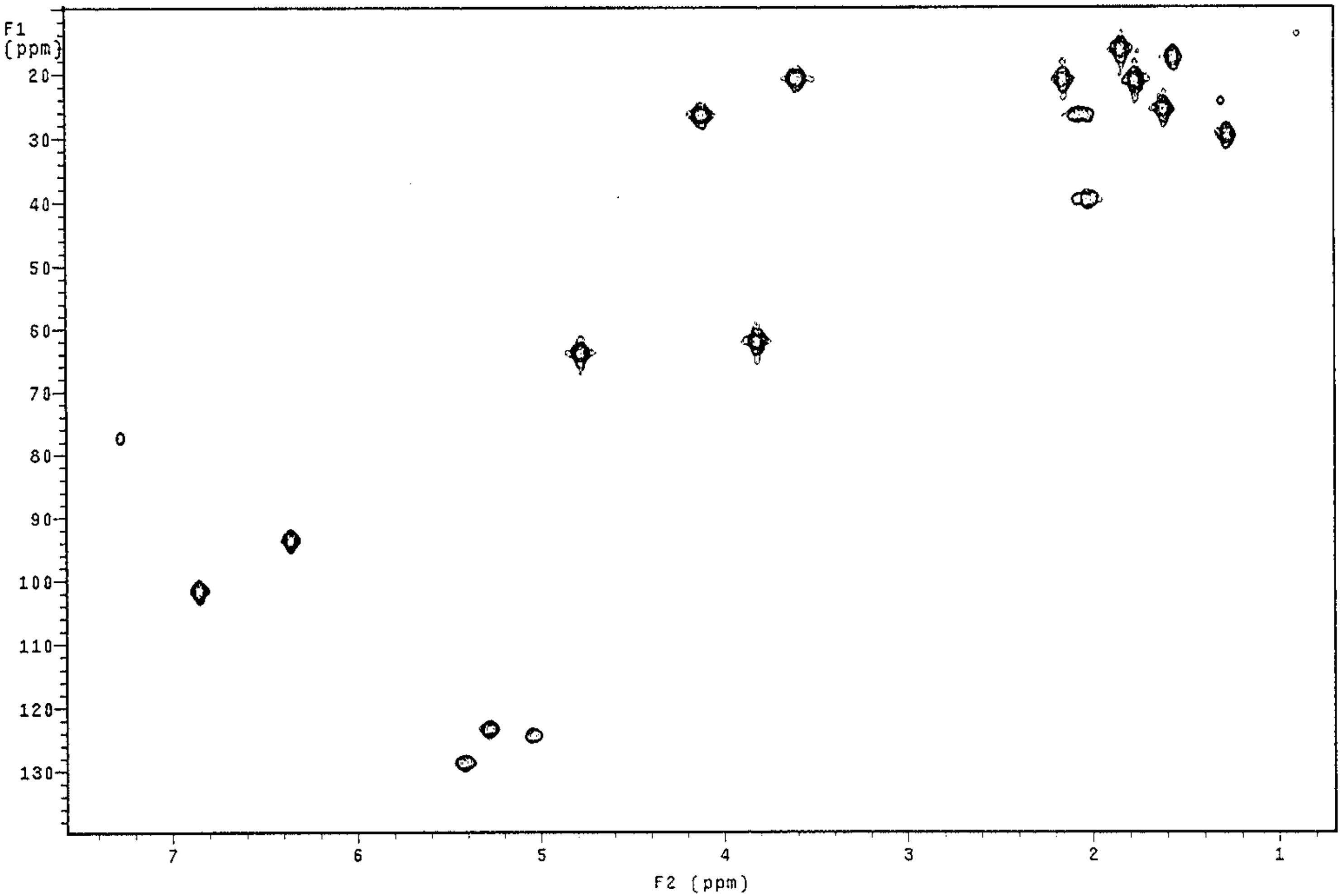


Figure 95 2D HMQC spectrum of **PGC12**

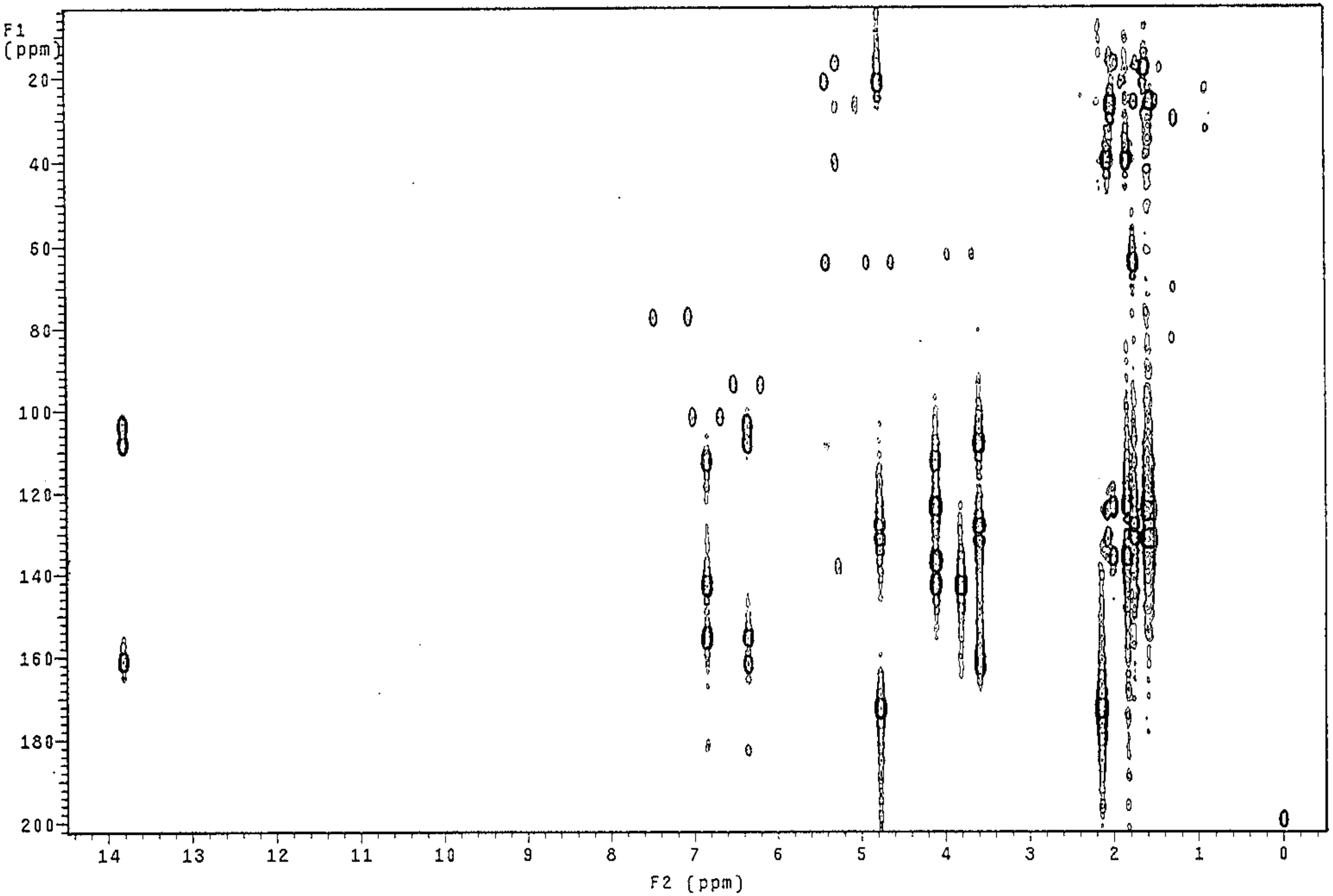


Figure 96 2D HMBC spectrum of **PGC12**

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