CHEMICAL CONSTITUENTS OF THE STEMS OF *DERRIS SCANDENS* AND STRUCTURAL MODIFICATION OF ISOFLAVONES FOR DRUG DISCOVERY

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A THESIS PRESENTED TO RAMKHAMHAENG UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE
(APPLIED CHEMISTRY)
2017

ส่วนประกอบทางเคมีของลำต้นเถาวัลย์เปรียงและการปรับเปลี่ยนโครงสร้างสารไอโซฟลาโวนเพื่อการค้นพบยา

ยุทธนา สิริวัฒนเสถียร

วิทยานิพนธ์เสนอต่อมหาวิทยาลัยรามคำแหง
เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญา
วิทยาศาสตรมหาบัณฑิต (เคมีประยุกต์)
ปีการศึกษา 2560

Thesis Title	Chemical Constituents of the Stems of *Derris scandens* and Structural Modification of Isoflavones for Drug Discovery
Student's Name	Mr. Yuttana Siriwattanasathien Department of Chemistry, Faculty of Science
Advisory Committee	Prof. Dr. Apichart Suksamrarn Chairperson Assoc. Prof. Dr. Thitima Rukachaisirikul

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Ramkhamhaeng University approved this thesis as a partial fulfillment of the requirements for the degree of Master of Science (Applied Chemistry).

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ABSTRACT

Thesis Title	Chemical Constituents of the Stems of *Derris scandens* and Structural Modification of Isoflavones for Drug Discovery
Student's Name	Mr. Yuttana Siriwattanasathien
Degree Sought	Master of Science
Field of Study	Applied Chemistry
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Advisory Committee

1. Prof. Dr. Apichart Suksamrarn — Chairperson
2. Assoc. Prof. Dr. Thitima Rukachaisirikul

Investigation of the stems of *Derris scandens* (Roxb.) Benth. has led to the isolation of seven known isoflavones, derrisisoflavone A (**1**), 5,7,4′-trihydroxy-6,8-diprenylisoflavone (**7**), lupalbigenin (**8**), scandinone (**9**), scanderone (**28**), osajin (**44**) and scandenin (**51**). The structure of these compounds were identified by comparison of spectroscopic data and some physical data with those of reported values.

Compounds **1**, **8** and **44** were subjected to structrual modification. The synthesized analogues included derrisisoflvone A 7-*O*-acetate (**124**), derrisisoflavone A 4′-*O*-acetate (**125**), derrisisoflavone A 7,4′-di-*O*-acetate (**126**), lupalbigenin 7-*O*-acetate (**127**), lupalbigenin 4′-*O*-acetate (**128**),

lupalbigenin 7,4′-di-*O*-acetate (**129**), osajin 4′-*O*-acetate (**130**), derrisisoflavone A 7-*O*-methyl ether (**131**), derrisisoflavone A 4′-*O*-methyl ether (**132**), derrisisoflavone A 7,4′-di-*O*-methyl ether (**133**), lupalbigenin 7-*O*-methyl ether (**134**), lupalbigenin 7,4′-di-*O*-methyl ether (**135**), 4′-*O*-methylosajin (**43**), tetrahydroderrisisoflavone A (**136**), hexahydroderrisisoflavone A (**137**), dihydrolupalbigenin (**138**), tetrahydrolupalbigenin (**139**), hexahydrolupalbigenin (**140**), tetrahydroosajin (**141**), hexahydroosajin (**142**), tetrahydrolupalbigenin 7-*O*-methyl ether (**143**), derrisisoflavone A 7-*O*-propanoate (**144**), derrisisoflavone A 4′-*O*-propanoate (**145**), derrisisoflavone A 7,4′-di-*O*-propanoate (**146**), 5′-nitrolupalbigenin (**147**), 2‴,3‴-epoxylupalbigenin (**148**), 2″,3″,2‴,3‴-diepoxylupalbigenin (**149**), lupalbigenin 7-*O*-benzoate (**150**), lupalbigenin 7,4′-di-*O*-benzoate (**151**), 7-*O*-propargyllupalbigenin (**152**), **7,**4′-di-*O*-propargyllupalbigenin (**153**) and 7-*O*-[1‴′-(carboxymethyl)-1‴′,*H*-3‴′,4‴′,5‴′-triazole]lupalbigenin (**155**). The isolated compounds and the modified analogues were subjected to butyrylcholinesterase inhibitory activity. Compound **136** exhibited the highest anti-butyrylcholinesterase activity (IC_{50} 2.53 μM) among the derrisisoflaven series, followed by compounds **124**, **144, 133**, and **125** (IC_{50} 6.07, 10.31, 12.58, and 16.04 μM, respectively) and the activity was higher than the parent compound **1**. Compound **138** exhibited activity higher (IC_{50} 0.64 μM) than the parent compound **8** and was the analaogue that exhibited the highest anti-butyrylcholinesterase inhibitory activity evaluations in this study.

Among them, compounds **138** and **136** exhibited significant activity of 4.8 and 1.2-fold, respectively, higher than that of reference anti-Alzheimer drug, galantamine.

บทคัดย่อ

ชื่อเรื่องวิทยานิพนธ์ ส่วนประกอบทางเคมีของลำต้นเถาวัลย์เปรียงและการปรับเปลี่ยนโครงสร้างสารไอโซฟลาโวนเพื่อการค้นพบยา

ชื่อผู้เขียน นายยุทธนา สิริวัฒนเสถียร

ชื่อปริญญา วิทยาศาสตรมหาบัณฑิต

สาขาวิชา เคมีประยุกต์

ปีการศึกษา 2560

คณะกรรมการที่ปรึกษาวิทยานิพนธ์

1. ศาสตราจารย์ ดร. อภิชาต สุขสำราญ ประธานกรรมการ
2. รองศาสตราจารย์ ดร. ธิติมา รุกขไชยศิริกุล

การศึกษาส่วนประกอบทางเคมีของลำต้นของเถาวัลย์เปรียง (*Derris scandens* (Roxb.) Benth.) สามารถแยกสารกลุ่มไอโซฟลาโวนที่เคยพบมาแล้ว 7 ชนิด คือ derrisisoflavone A (**1**), 5,7,4′-trihydroxy-6,8-diprenylisoflavone (**7**), lupalbigenin (**8**), scandinone (**9**), scanderone (**28**), osajin (**44**) และ scandenin (**51**) โครงสร้างของสารเหล่านี้หาได้จากการเปรียบเทียบข้อมูลทางสเปกโทรสโกปีและข้อมูลทางกายภาพที่หาได้กับข้อมูลที่มีผู้รายงานไว้

สาร **1**, **8** และ **44** เป็นสารที่ใช้ในการปรับเปลี่ยนโครงสร้างได้แอนาลอก คือ derrisisoflvone A 7-*O*-acetate (**124**), derrisisoflavone A 4′-*O*-acetate (**125**), derrisisoflavone A 7,4′-di-*O*-acetate (**126**), lupalbigenin 7-*O*-acetate (**127**), lupalbigenin 4′-*O*-acetate (**128**), lupalbigenin 7,4′-di-*O*-acetate (**129**), osajin 4′-*O*-acetate (**130**), derrisisoflavone A 7-*O*-methyl ether (**131**), derrisisoflavone A 4′-*O*-methyl ether (**132**), derrisisoflavone A 7,4′-di-*O*-methyl ether (**133**), lupalbigenin 7-*O*-methyl ether (**134**), lupalbigenin 7,4′-di-*O*-methyl ether (**135**), 4′-*O*-methylosajin (**43**),

tetrahydroderrisisoflavone A (**136**), hexahydroderrisisoflavone A (**137**), dihydrolupalbigenin (**138**), tetrahydrolupalbigenin (**139**), hexahydrolupalbigenin (**140**), tetrahydroosajin (**141**), hexahydroosajin (**142**), tetrahydrolupalbigenin 7-*O*-methyl ether (**143**), derrisisoflavone A 7-*O*-propanoate (**144**), derrisisoflavone A 4′-propanoate (**145**), derrisisoflavone A 7,4′-di-*O*-propanoate (**146**), 5′-nitrolupalbigenin (**147**), 2‴,3‴-epoxylupalbigenin (**148**), 2″,3″,2‴,3‴-diepoxylupalbigenin (**149**), lupalbigenin 7-*O*-benzoate (**150**), lupalbigenin 7,4′-di-*O*-benzoyl ester (**151**), 7-*O*-propargyllupalbigenin (**152**), **7,**4′-di-*O*-propargyllupalbigenin (**153**) และ 7-*O*-[1⁗-(carboxymethyl)-1⁗,*H*-3⁗,4⁗,5⁗-triazole]lupalbigenin (**155**) ในกลุ่มได้นำสารที่แยกได้และแอนาลอกทดสอบฤทธิ์ทางชีวภาพคือ ฤทธิ์การยับยั้งเอนไซม์บิวทีริลโคลีนเอสเทอเรส พบว่าสาร **136** มีฤทธิ์ในการยับยั้งต่อเอนไซม์บิวทีริลโคลีนเอสเทอเรสมากที่สุดที่ค่า IC_{50} 2.53 μM ตามด้วยสาร **124**, **144**, **133** และ **125** แสดงค่า IC_{50} เท่ากับ 6.07, 10.31, 12.58 และ 16.04 μM ตามลำดับ และแสดงฤทธิ์ในการยับยั้งมากกว่าสารตั้งต้น **1** และสารประกอบ **138** มีฤทธิ์ IC_{50} 0.64 μM ซึ่งมากกว่าสารต้นต้น **8** และเป็นสารที่มีฤทธิ์ต้านเอนไซม์บิวทีริลโคลีนเอสสูงสุดในการศึกษาครั้งนี้ สาร **138** และ **136** แสดงผลการยับยั้งได้ดีเป็น 4.8 และ 1.2 เท่าตามลำดับ เมื่อเปรียบเทียบกับกาลานทามีนซึ่งใช้เป็นยาต้านอัลไซเมอร์มาตรฐาน

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Yuttana Siriwattanasathien

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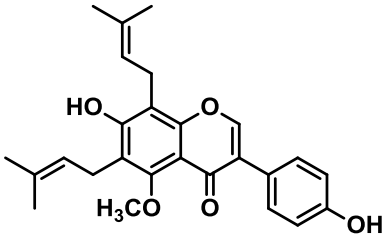
CHAPTER 1

INTRODUCTION

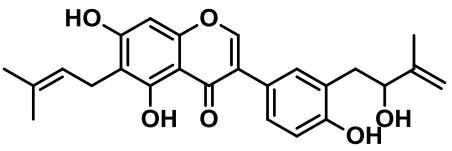
The genus *Derris* belongs to the family Fabaceae, comprising approximately 92 species distributed throughout Southest Asian and Southwest Pacific islands. There are 17 species of the genus *Derris* in Thailand.[1] *Derris scandens* Benth. is a well-known folk medicinal plant and commonly knows as 'Tao-Wan-Priang'. Its dried stem has been used as an expectorant, antitussive, diuretic, and antidysentery agent and for the treatment of muscle aches and pains. Some of the isolates from *D. scandens* exhibited anti-dermatophyte activity, hypotensive, anti-hypertensive, anti-HIV, antibacterial, anti-inflammatory and α-glucosidase enzyme inhibitory activities.[2-7]

D. scandens has been reported to process several other biological activities and chemical constituents as follows.

In 1999, Sekine *et al.*[2] investigated the chemical constituents of the EtOH extract of the stems of *D. scandens*, and six new diprenylisoflavones, derrisisoflavone A (**1**), derrisisoflavone B (**2**), derrisisoflavone C (**3**), derrisisoflavone D (**4**), derrisisoflavone E (**5**), derrisisoflavone F (**6**), together with six known isoflavones, 5,7,4′-trihydroxy-6,8-diprenylisoflavone (**7**), lupalbigenin (**8**), scandinone (**9**), erysenegalensein E (**10**), lupinisol (**11**) and lupinisoflavone G (**12**) were isolated. These compounds show anti-dermatophyte activity.



(1)



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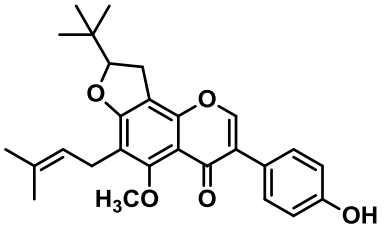

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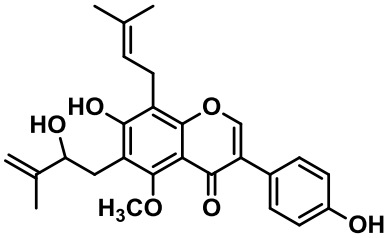

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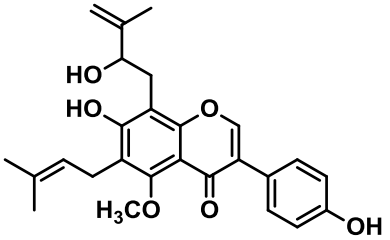

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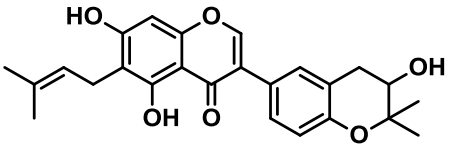

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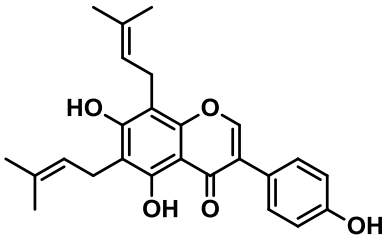

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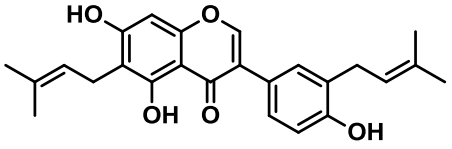

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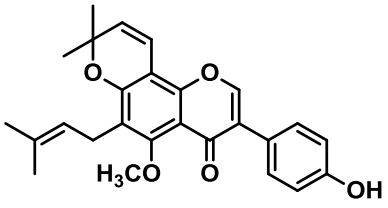

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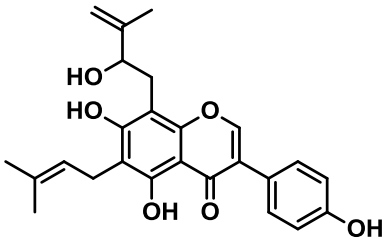

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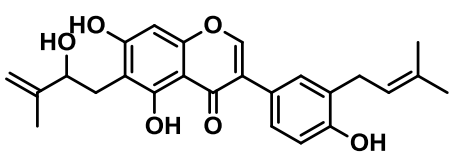

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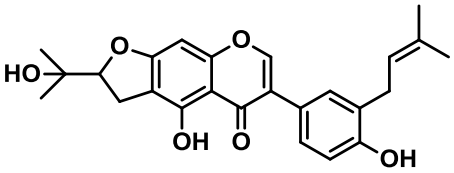
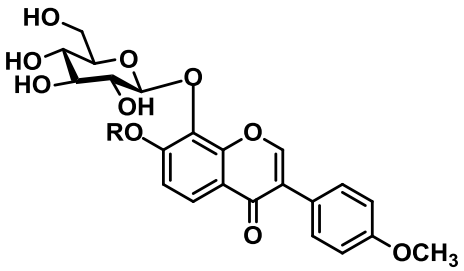


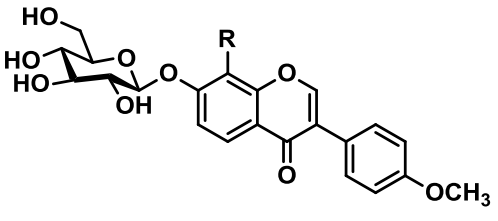
(**12**)

In 2002, Rukachaisirikul *et al.*[3] studied the water extract of the stems of *D. scandens*. This led to the isolation and identification of derriscandenoside A (**13**), derriscandenoside B (**14**), derriscandenoside C (**15**), derriscandenoside D (**16**), derriscandenoside E (**17**), derrisscanoside A (**18**), derrisscanoside B (**19**), formononetin 7-*O*-*β*-glucopyranoside (**20**), 8-hydroxy-4′,7-dimethoxyisoflavone 8-*O*-*β*-glucopyranoside (**21**), 7-hydroxy-4′-8-dimethoxyisoflavone 7-*O*-*β*-glucopyranoside (**22**), diadzein 7-*O*-[*α*-rhamopyransoyl-(1⟶6)-*β*-glucopyranoside (**23**), formononetin 7-*O*-[*α*-rhamopyransoyl-(1⟶6)-*β*-glucopyranoside (**24**), and genistein 7-*O*-[*α*-rhamopyransoyl-(1⟶6)-*β*-glucopyranoside (**25**) were isolated. These rhamnosyl-(1⟶6)-glycosyl isoflavones exhibited hypotensive activity.



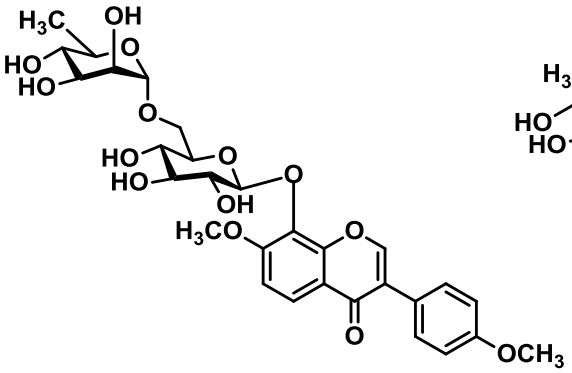
(**13**) R = H

(**21**) R= CH_3



(**20**) R = H

(**22**) R= OCH_3



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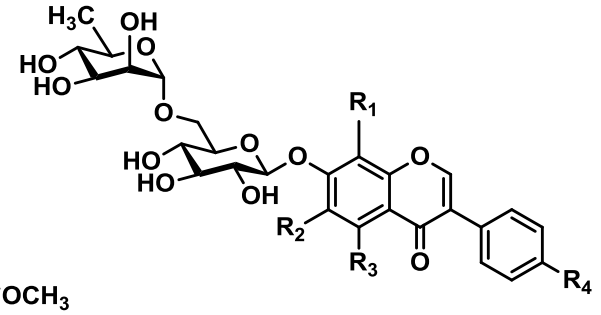


(**14**) $R_1 = OH, R_2 = R_3 = H, R_4 = OCH_3$

(**16**) $R_1 = R_3 = H, R_2 = R_4 = OCH_3$

(**17**) $R_1 = H, R_2 = R_4 = OCH_3, R_3 = OH$

(**18**) $R_1 = R_2 = R_3 = H, R_4 = OCH_3$

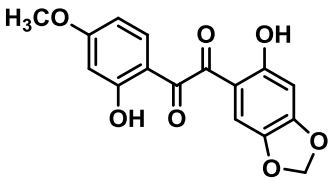
(**19**) $R_1 = R_4 = OCH_3, R_2 = R_3 = H$

(**23**) $R_1 = R_2 = R_3 = H, R_4 = OH$

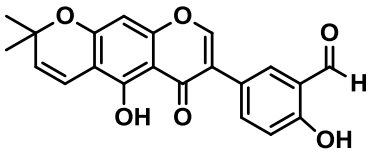
(**24**) $R_1 = R_2 = R_3 = H, R_4 = OCH_3$

(**25**) $R_1 = R_2 = H, R_3 = R_4 = OH$

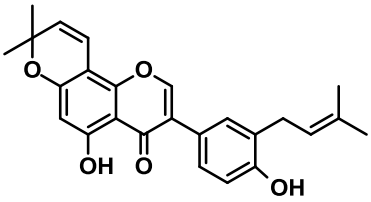
In 2004, Mahabusarakam *et al.*[4] investigated the chemical constituents of the methanol extract of the stems of *D. scandens*, and one new benzil derivative, scandione (**26**), and two new isoflavones, scandenal (**27**), scanderone (**28**), with fifteen known compounds flamichapparin B (**29**), lupalbigenin (**8**), flemichapparin C (**30**), isorobustone (**31**), 5-hydroxy-2″,2″-dimethylchromeno-[6,7:5″,6‴]-2‴,2‴-dimethylchromeno[3′,4′:5‴,6‴]isoflavone (**32**), ulexone A (**33**), chandalone (**34**), maackiain (**35**), isochandalone (**36**), scandinone (**9**), derrisisoflavone A (**1**), santal (**37**), lupiwighteone (**38**), 3′-methylorobol (**39**) and genistein (**40**). Compounds **1**, **9**, **27-29**, **34-35** and **37-38** exhibited hypotensive activity.



(**26**)



(**27**)



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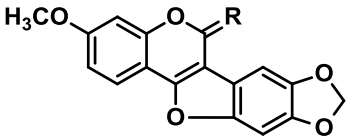
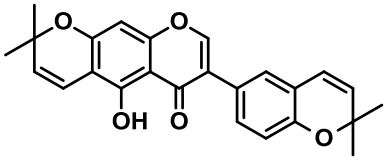
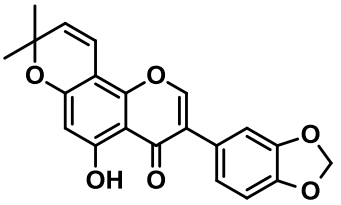


(**29**) R = H_2

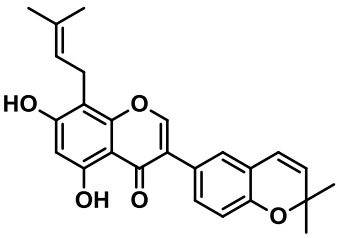
(**30**) R = O



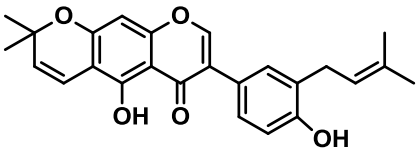
(**31**)



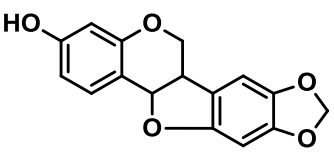
(**32**)



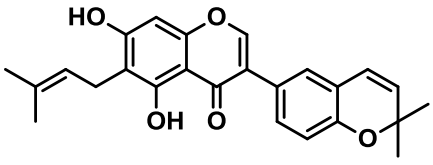
(**33**)



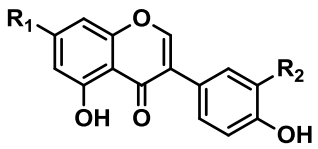
(**34**)



(**35**)



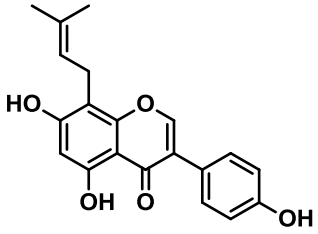
(**36**)



(**37**) $R_1 = OCH_3$, $R_2 = OH$

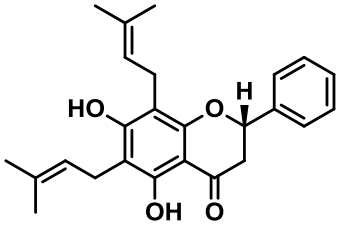
(**39**) $R_1 = OH$, $R_2 = OCH_3$

(**40**) $R_1 = OH$, $R_2 = H$

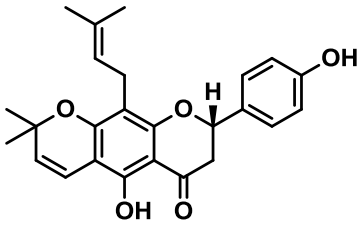


(**38**)

In 2006, Ganapaty *et al.*[5] investigated the chemical constituents of the chloroform extract of the leaves and roots of *D. scandens*, and two known flavonoids, ovalifavanone (**41**) and lupinifolin (**42**). These flavonoids exhibited anti-inflammatory activity.



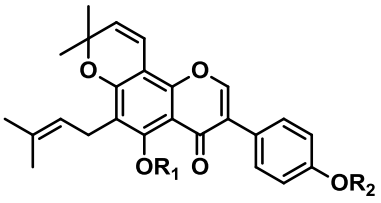
(**41**)



(**42**)

In 2007, Rao *et al.*[6] studied the hexane and chlroform extracts of the whole plant of *D. scandens*. This led to the isolation and identification of 4′-*O*-methylosajin (**43**), osajin (**44**), 4′-*O*-methylscandinone (**45**), 5,7,4′-trihydroxy-6,8-diprenylisoflavone (**7**), isoscandinone (**46**), scandenin A (**47**), scandinin B (**48**), scandenone (**49**), scandinone (**9**) lupalbigenin (**8**) derrisisoflavone A (**1**),

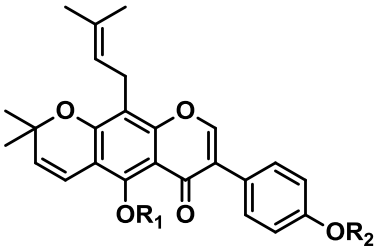
derrisisoflavone C (**3**), 4′,4-*O*-dimethylscandenin (**50**) and scandenin (**51**). Compounds **7**, **43-44** and **45** exhibited α-glucosidase inhibitory activity.



(**43**) R_1 = H, R_2 = CH_3

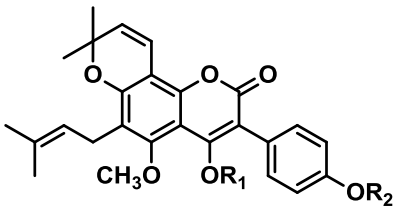
(**44**) R_1 = H, R_2 = H

(**45**) R_1 = CH_3, R_2 = CH_3



(**46**) R_1 = CH_3, R_2 = H

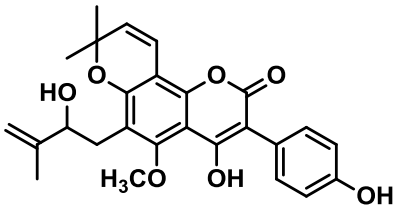
(**49**) R_1 = H, R_2 = H



(**47**) R_1 = H, R_2 = CH_3

(**50**) R_1 = CH_3, R_2 = CH_3

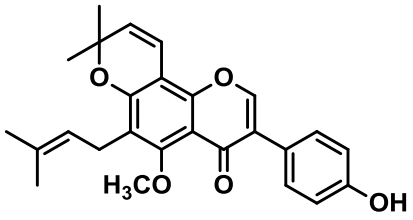
(**51**) R_1= H, R_2 = H



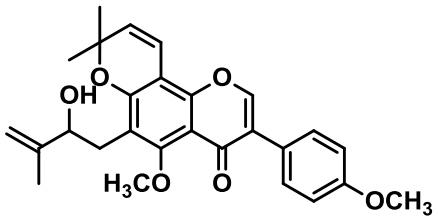
(**48**)

In 2010, Babu *et al.*[7] studied the hexane extract of the whole plant of *D. scandens* and one new isoflavone derivative, scandinone A (**52**), together with eleven known isoflavones, 4′-*O*-methylosajin (**43**), osajin (**44**), 4′-*O*-methyl scandinone (**53**), derrisisoflavone A (**1**), 5,7,4′-trihydroxy-6,8-diprenylisoflavone (**7**), scandenone (**49**), scandinone (**9**), 4′,4-*O*-dimethylscandenin (**50**),

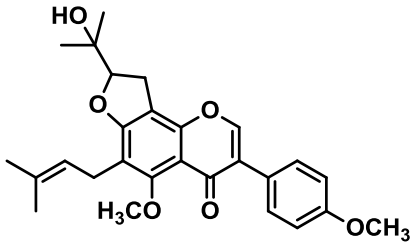
derrisisoflavone D (**4**), 4′-*O*-methylsenegalensein (**54**) and scandenin B (**55**). Compounds **1**, **4**, **7**, **9**, **49**, **52** and **54** exhibited α-glucosidase inhibitory activity.



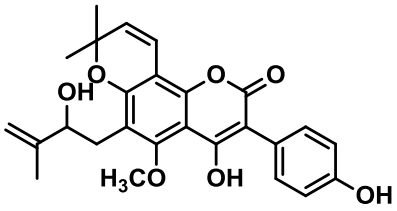
(**52**)



(**53**)



(**54**)



(**55**)

Apart from *D. scandens*, other *Derris* species have been investigated for chemical constituents and some of the isolated compounds were subjected to biological testing. Isoflavones isolated from *Derris* species are shown in Tables 1-10.

Table 1 Rotenoids from *Derris* species

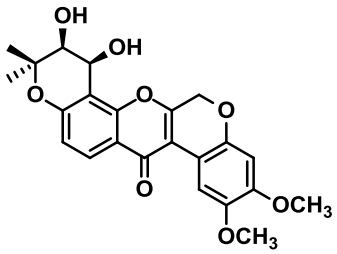
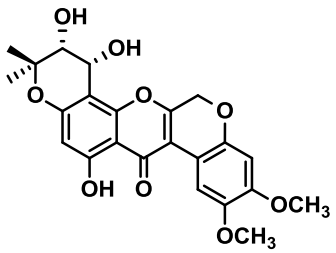
Compound [Source]	Extract	Biological activity	Year [Ref.]
 4′,5′-Dihydroxy-6a,12a-dehydrodeguelin (**56**) [*D. elliptica*]	EtOH	-	2008 [9]
 11′,4′,5′-Trihydroxy-6a,12a-dehydrodeguelin (**57**) [*D. elliptica*]	EtOH	-	2008 [9]

Table 1 (continued)

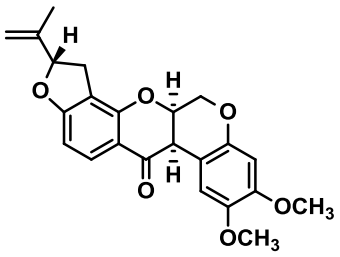
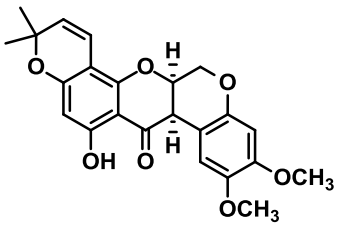
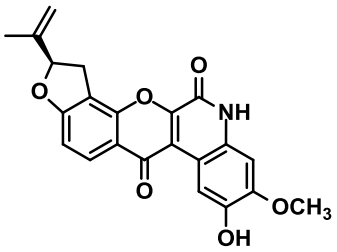
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Rotenone (**58**) [*D. elliptica*]	EtOH	-	2008 [9]
 Deguelin (**59**) [*D. elliptica*]	EtOH	-	2008 [9]
 2-Hydroxy-5-aminorotenonone (**60**) [*D. elliptica*]	EtOH	-	2009 [10]

Table 1 (continued)

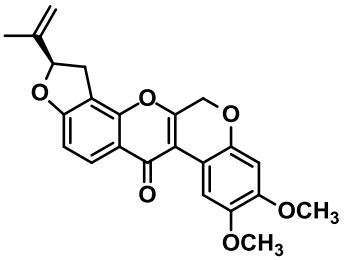
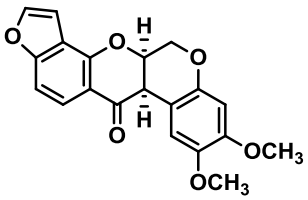
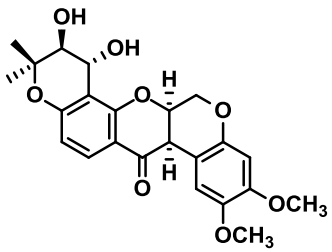
Compound [Source]	Extract	Biological activity	Year [Ref.]
 5′*R*-6a,12a-Dehydrorotenone (**61**) [*D. elliptica*][a] [*D. malaccensis*][b]	EtOH[a,b]	Antibacterial activity against *Helicobacter pylori*[b]	2012 [11][a] 2014 [16][b]
 Elliptone (**62**) [*D. malaccensis*]	MeOH	Antibacterial activity against *Helicobacter pylori*	2014 [16]
 Derrisin (**63**) [*D. malaccensis*]	MeOH	-	2014 [16]

Table 1 (continued)

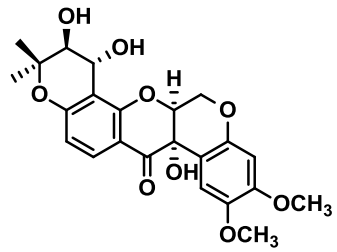
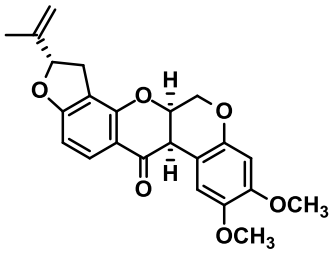
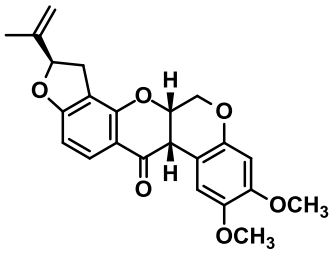
Compound [Source]	Extract	Biological activity	Year [Ref.]
 4′,5′-Dihydroxytephrosin (**64**) [*D. malaccensis*]	MeOH	-	2014 [16]
 Rotenone (**65**) [*D. malaccensis*]	MeOH	Antibacterial activity against *Helicobacter pylori*	2014 [16]
 Rotenolone (**66**) [*D. malaccensis*]	MeOH	Antibacterial activity against *Helicobacter pylori*	2014 [16]

Table 1 (continued)

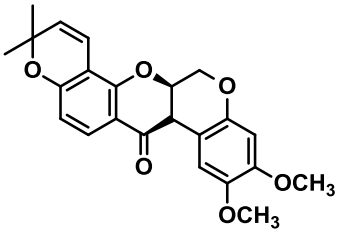
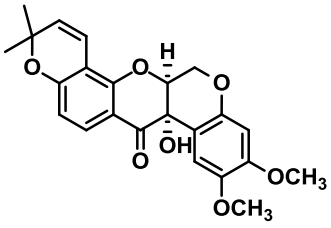
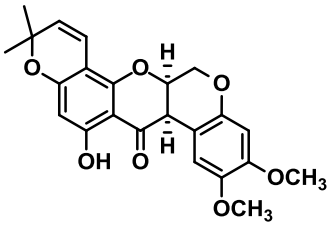
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Deguelin (**67**) [*D. malaccensis*]	MeOH	Antibacterial activity against *Helicobacter pylori*	2014 [16]
 Tephrosin (**68**) [*D. malaccensis*]	MeOH	Antibacterial activity against *Helicobacter pylori*	2014 [16]
 Toxicarol (**69**) [*D. malaccensis*]	MeOH	Antibacterial activity against *Helicobacter pylori*	2014 [16]

Table 1 (continued)

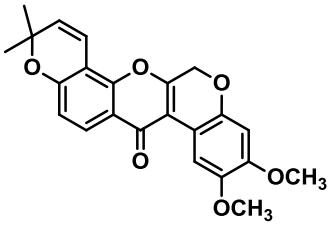
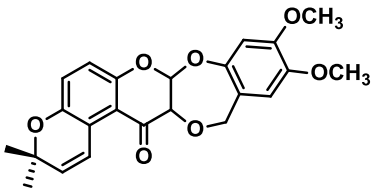
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Dehydrodeguelin (**70**) [*D. malaccensis*]	MeOH	Antibacterial activity against *Helicobacter pylori*	2014 [16]
 13-*Homo*-13-oxa-6a,12a-dehydrodeguelin (**71**) [*D. malaccensis*]	MeOH	Antibacterial activity against *Helicobacter pylori*	2014 [16]

Table 2 Coumaronochromones from *Derris* species

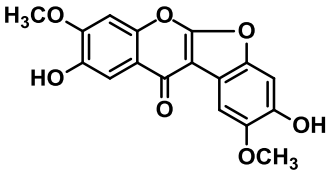
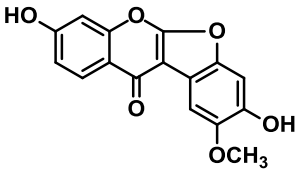
Compound [Source]	Extract	Biological activity	Year [Ref.]
 6,4′-Dihydroxy-7,5′-dimethoxycoumaronochromone (**72**) [*D. elliptica*]	EtOH	-	2012 [11]
 7,4′-Dihydroxy-5′-methoxycoumaronochromone (**73**) [*D. elliptica*]	EtOH	Exhibited moderate insecticidal activity against larvae	2012 [11]

Table 3 Pterocarps from *Derris* species

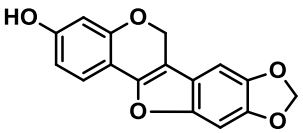
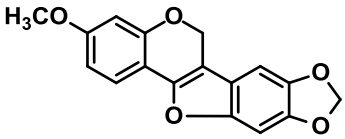
Compound [Source]	Extract	Biological activity	Year [Ref.]
 3-Hydroxy-8,9-methylenedioxypterocarp-6a-ene (**74**) [*D. elliptica*]	EtOH	Exhibited moderate insecticidal activity against larvae	2012 [11]
 Flemichapparin-B (**75**) [*D. elliptica*]	EtOH	-	2012 [11]

Table 4 Pterocarpans from *Derris* species

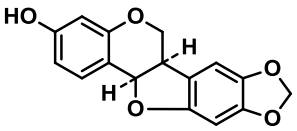
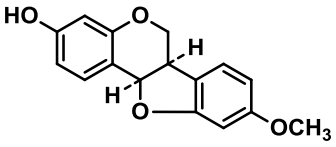
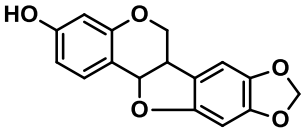
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Maackiain (**76**) [*D. indica*]	CH_2Cl_2	Antibacterial activity	2006 [13]
 Medicarpin (**77**) [*D. indica*]	CH_2Cl_2	-	2006 [13]
 7-Hydroxy-4′,5′-methylenedioxypterocarpan (**78**) [*D. elliptica*]	EtOH	-	2012 [11]

Table 5 Flavones from *Derris* species

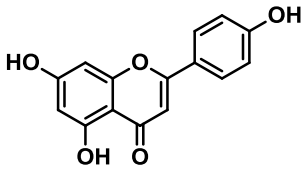
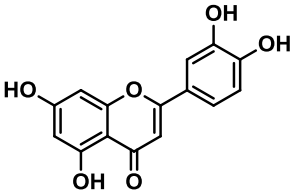
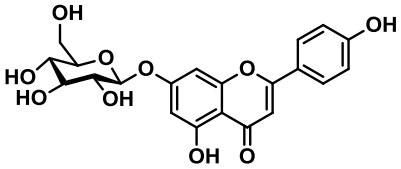
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Apigenin (**79**) [*D. elliptica*]	EtOH	Exhibited moderate insecticidal activity against larvae	2012 [11]
 Luteolin (**80**) [*D. elliptica*]	EtOH	-	2012 [11]
 Apigenin 7-*O*-*β*-D-glucoside (**81**) [*D. elliptica*]	EtOH	-	2012 [11]

Table 5 (continued)

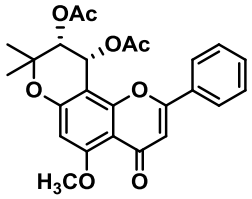
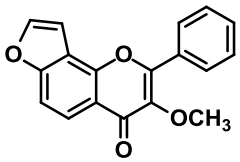
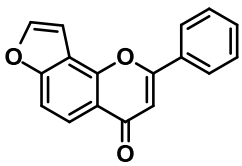
Compound [Source]	Extract	Biological activity	Year [Ref.]
 3-Methoxy-(3″,4″-dihydro-3″,4″-diacetoxy)-2″,2″-dimethylpyrano-(7,8:5″,6″)-Flavone (**82**) [*D. indica*]	CH_2Cl_2	Antibacterial activity	2006 [13]
 Karanjin (**83**) [*D. indica*]	CH_2Cl_2[a] EtOAc[b] MeOH[c]	Inhibit BSA–methylglyoxal antiglycation model[b] anticancer activity[c]	2006 [13][a] 2014 [14][c] 2014 [15][b]
 Lacheolatin B (**84**) [*D. indica*]	CH_2Cl_2[a] EtOAc[b]	Antibacterial activity[a]	2006 [13][a] 2014 [14][b]

Table 5 (continued)

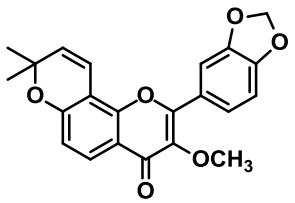
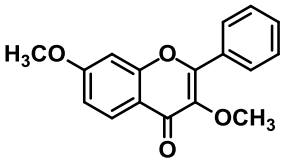
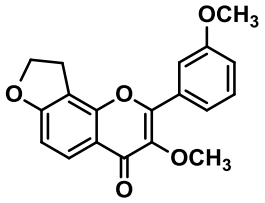
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Pongachromene (**85**) [*D. indica*]	CH_2Cl_2	-	2006 [13]
 3,7-Dimethoxyflavone (**86**) [*D. elliptica*]	CH_2Cl_2	Antibacterial activity	2006 [13]
 Pachycarin D (**87**) [*D. indica*]	CH_2Cl_2	-	2006 [13]

Table 5 (continued)

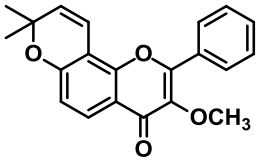
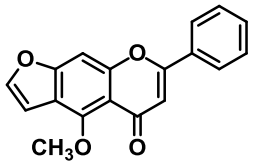
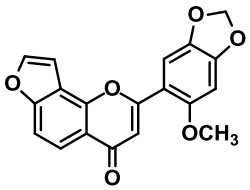
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Karanjachromene (**88**) [*D. indica*]	CH_2Cl_2	Antibacterial activity	2006 [13]
 Pinnatin (**89**) [*D. indica*]	CH_2Cl_2	Antibacterial activity	2006 [13]
 2′-Methoxy-4′,5′-methylenedioxyfurano [7,8:4″,5″]-flavone (**90**) [*D. indica*]	CH_2Cl_2	-	2006 [13]

Table 5 (continued)

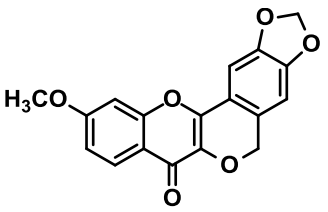
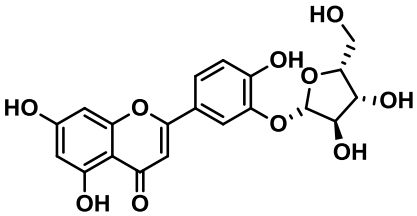
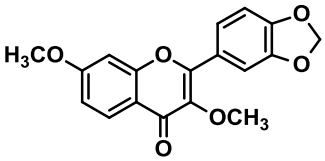
Compound [Source]	Extract	Biological activity	Year [Ref.]
 3,4-Methylenedioxy-10-methoxy-7-oxo[2]benzopyrano[4,3-b]benzopyran (**91**) [*D. indica*]	CH_2Cl_2	Antibacterial activity	2006 [13]
 Leutolin-3′-*O*-xilofuranose (**92**) [*D. brevipes*]	MeOH	Anticancer activity Anti-inflammation Antioxidant activity	2014 [12]
 Desmethoxykanugin (**93**) [*D. indica*]	MeOH	Anticancer activity	2014 [14]

Table 5 (continued)

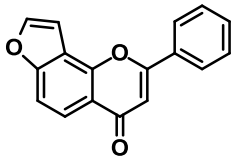
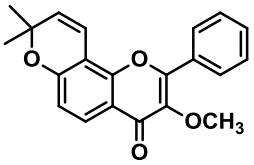
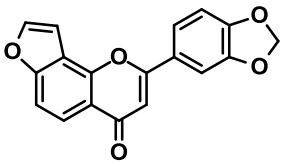
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Lanceolatin B (**94**) [*D. indica*]	MeOH	Anticancer activity	2014 [14]
 Pongaflavone (**95**) [*D. indica*]	EtOAc[a] MeOH[b]	Anticancer activity[b]	2014 [14][b] 2014 [15][a]
 Pongaglabrone (**96**) [*D. indica*]	EtOAc[a] MeOH[b]	Anticancer activity[b]	2014 [14][b] 2014 [15][a]

Table 5 (continued)

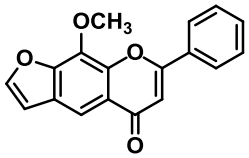
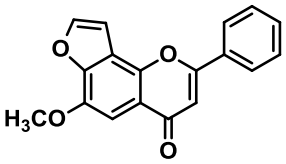
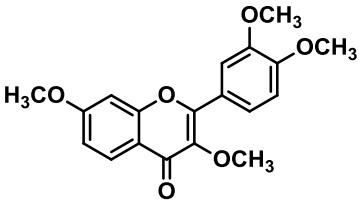
Compound [Source]	Extract	Biological activity	Year [Ref.]
 8-Methoxyfurano (6,7:4″,5″)-flavone (**97**) [*D. indica*]	MeOH	Anticancer activity	2014 [14]
 Kanjone (**98**) [*D. indica*]	MeOH	Anticancer activity	2014 [14]
 Fisetin tetramethyl ether (**99**) [*D. indica*]	EtOAc	-	2014 [15]

Table 5 (continued)

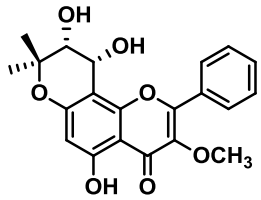
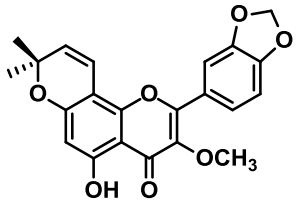
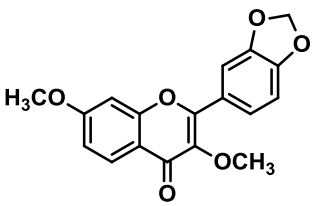
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Derrisin B (**100**) [*D. indica*]	EtOAc	Inhibit BSA–methylglyoxal antiglycation model	2014 [15]
 Pongachromene (**101**) [*D. indica*]	EtOAc	-	2014 [15]
 Desmethoxykanugin (**102**) [*D. indica*]	CH_2Cl_2[a] EtOAc[b]	Antibacterial activity[a]	2006 [13][a] 2014 [15][b]

Table 5 (continued)

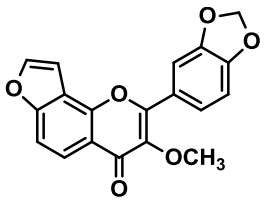
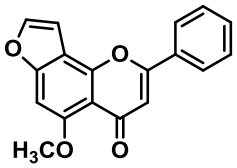
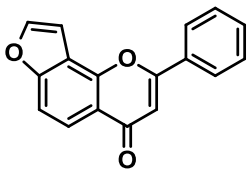
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Pongapin (**103**) [*D. indica*]	EtOAc	Inhibit BSA–methylglyoxal antiglycation model	2014 [15]
 Pongaglabol methyl ether (**104**) [*D. indica*]	EtOAc	-	2014 [15]
 Lacneolatin B (**105**) [*D. indica*]	EtOAc	Inhibit BSA–methylglyoxal antiglycation model	2014 [15]

Table 5 (continued)

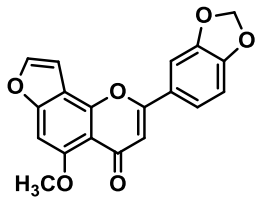
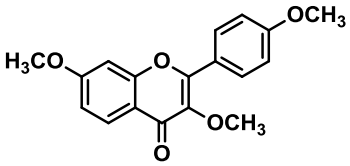
Compound [Source]	Extract	Biological activity	Year [Ref.]
 5-Methoxy-3″,4″-methylenedioxy(8,7,4″,5″)-flavone (**106**) [*D. indica*]	EtOAc	-	2014 [15]
 3,7-Dimethoxy-2-(4-methoxy phenyl)flavone (**107**) [*D. indica*]	EtOAc	-	2014 [15]

Table 6 Flavanonols from *Derris* species

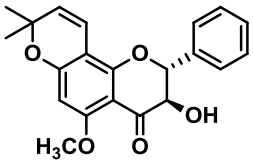
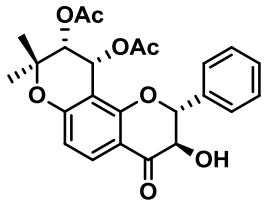
Compound [Source]	Extract	Biological activity	Year [Ref.]
 (2*R*,3*R*)-3-Hydroxy-5-methoxy-2″,2″-dimethylpyrano [7,8:5″,6″]-flavanone (**108**) [*D. indica*]	MeOH	Anticancer activity	2014 [14]
	EtOAc	-	2014 [15]
 Derrisin A (**109**) [*D. indica*]			

Table 7 Flavanones from *Derris* species

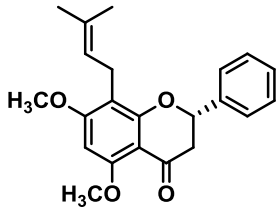
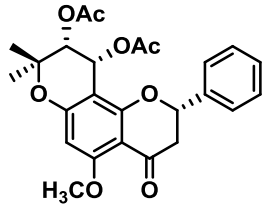
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Candidone (**110**) [*D. indica*]	MeOH	Anticancer activity	2014 [14]
 Derrivanone (**111**) [*D. indica*]	Hexane	Anticancer activity	2014 [15]

Table 8 Isoflavones from *Derris* species

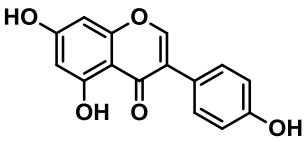
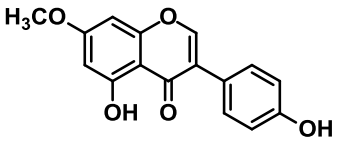
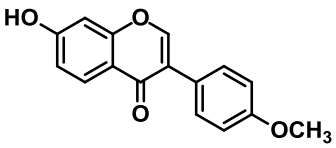
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Genistein (**112**) [*D. elliptica*]	EtOH	-	2012 [11]
 Prunetin (**113**) [*D. elliptica*]	EtOH	Exhibited moderate insecticidal activity against larvae	2012 [11]
 Formononetin (**114**) [*D. elliptica*]	EtOH	Exhibited moderate insecticidal activity against larvae	2012 [11]

Table 8 (continued)

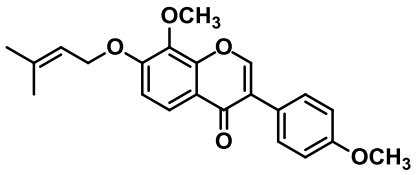
Compound [Source]	Extract	Biological activity	Year [Ref.]
 8,4′-Dimethoxy-7-*O*-γ, γ-dimethylallylisoflavone (**115**) [*D. indica*]	CH_2Cl_2	-	2006 [13]

Table 9 Chalcones from *Derris* species

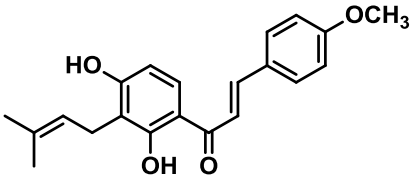
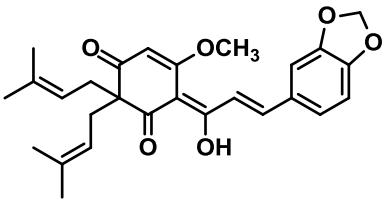
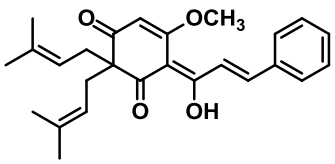
Compound [Source]	Extract	Biological activity	Year [Ref.]
 2′,4′-Dihydroxy-4-methoxy-3′-prenyl chalcone (**116**) [*D. brevipes*]	MeOH	Anti-inflammation Antioxidant activities	2014 [12]
 Derrischalcone (**117**) [*D. indica*]	Hexane	Anticancer activity	2014 [14]
 Iunicatachalcone (**118**) [*D. indica*]	MeOH	Anticancer activity	2014 [14]

Table 9 (continued)

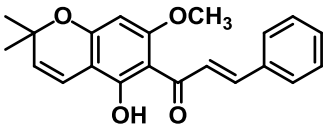
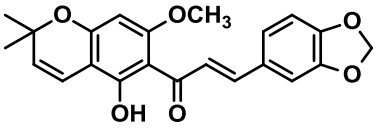
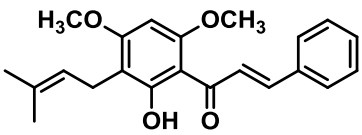
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Obovatachalcone (**119**) [*D. indica*]	MeOH	Anticancer activity	2014 [14]
 Glabrachromene (**120**) [*D. indica*]	MeOH	Anticancer activity	2014 [14]
 Ovalichalcone (**121**) [*D. indica*]	MeOH	Anticancer activity	2014 [14]

Table 9 (continued)

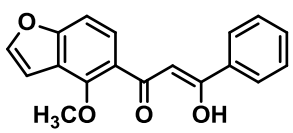
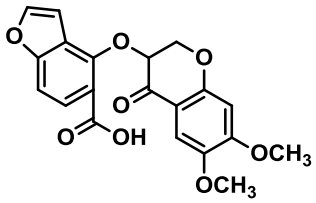
Compound [Source]	Extract	Biological activity	Year [Ref.]
 Pongamol (**122**) [*D. indica*]	MeOH	Anticancer activity	2014 [14]

Table 10 Tubaic acid from *Derris* species

Compound [Source]	Extract	Biological activity	Year [Ref.]
 Elliptoic acid (**123**) [*D. elliptica*]	EtOH	-	2009 [10]

CHAPTER 2

EXPERIMENTAL

General Techniques

1. Solvent

1.1 The organic solvents were commercial grade and were distilled prior to use for extraction, as eluent for thin layer and column chromatography. Analytical grade solvents were used for the synthesis.

2. Chromatography

2.1 Thin Layer Chromatography (TLC)

Techniques: One way, ascending.

Adsorbent: Silica gel 60 F_{254} pre-coated on aluminum plate (E. Merck) size 1 x 5 cm, 2 x 5 cm and 3 x 5 cm.

Detection on chromatography plate:

2.1.1 Ultraviolet light at 254 nm. The compound which contains unsaturated bonds especially conjugated system is visible as quenching spot under UV light at 254 nm.

2.1.2 Developing reagent: Anisaldehyde reagent consisted of *p*-methoxybenzaldehyde (3 ml), concentrated sulfuric acid (2 ml), water (2 ml) and absolute ethanol (90 ml). The spots of organic compounds give specific colors with this reagent after heating at 90-110 ^{o}C for 1-4 minutes.

2.2 Column Chromatography (CC)

2.2.1 Column Chromatography (CC)

Adsorbent: Unless indicated otherwise, silica gel with particle size less than 60-200 μm (SiliCycle Silica*Flash* G 60) was used throughout the experiments.

Packing method: Slurry packing.

Sample loading: The sample was dissolved in a small amount of suitable organic solvent, mixed with a small quantity of silica gel 60 with particle size 60-200 μm, air dried and added gently onto the top of column.

Elution: After loading of the sample, the column was eluted with suitable solvent system using isocratic or gradient technique.

2.2.2 Gel Filtration chromatography

Adsorbent: Sephadex LH-20 (Pharmacia)

Packing method: Gel filter was suspended in the eluent and left standing to swell for 24 hours prior to use. It was poured into the column and allowed to set tightly.

Sample loading: The sample was dissolved in a small amount of suitable organic solvent and added gently onto the top of column.

Elution: After loading of the sample, the column was eluted with suitable solvent system.

3. Physical Constant

Optical rotations were obtained using a JASCO-1020 polarimeter.

Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. The temperature was given in degree Celsius.

4. Spectroscopy

4.1 Infrared (IR) Spectra. IR spectra were recorded on a Perkin-Elmer FT-IR 400 Spectrometer. Spectra of solid sample were recorded as ATR.

4.2 Nuclear Magnetic Resonance (NMR) Spectra. 1D and 2D NMR spectra were measured with a Bruker AVANCE 400 NMR spectrometer, operating at 400 MHz (^{1}H) and 100 MHz (^{13}C).

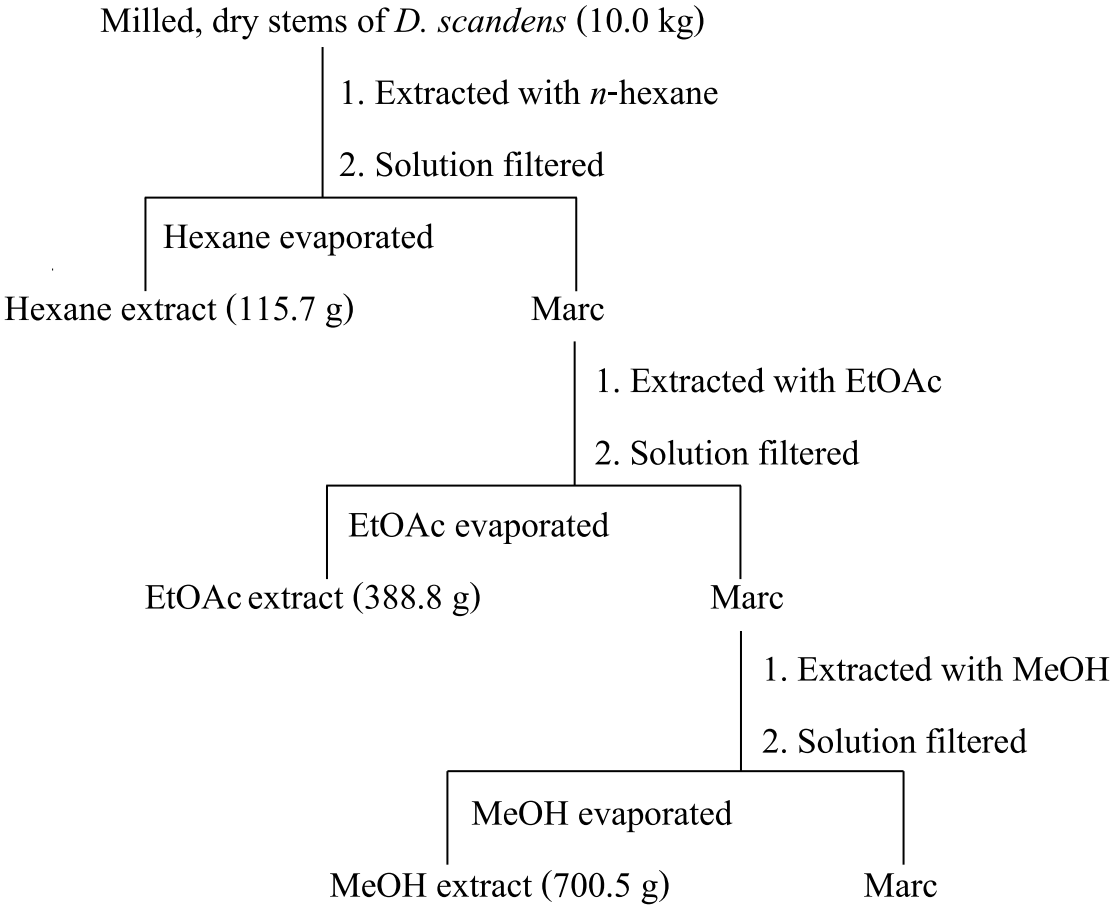
4.3 Mass Spectra. Electrospray ionization mass spectra (ESIMS) were determined on a Finnigan LC-Q mass spectrometer. The high resolution mass spectra were obtained using a Bruker micrOTOF-II mass spectrometer.

Source of Plant Materials

The dry stems of *Derris scandens* used in this study were purchased from Bansamunpaiosot herbal store, Bangkok in 2015. A voucher specimen (Apichart Suksamrarn No. 086) is deposited at the Faculty of Science, Ramkhamhaeng University.

Extraction and Isolation of the Stems of *Derris scandens*

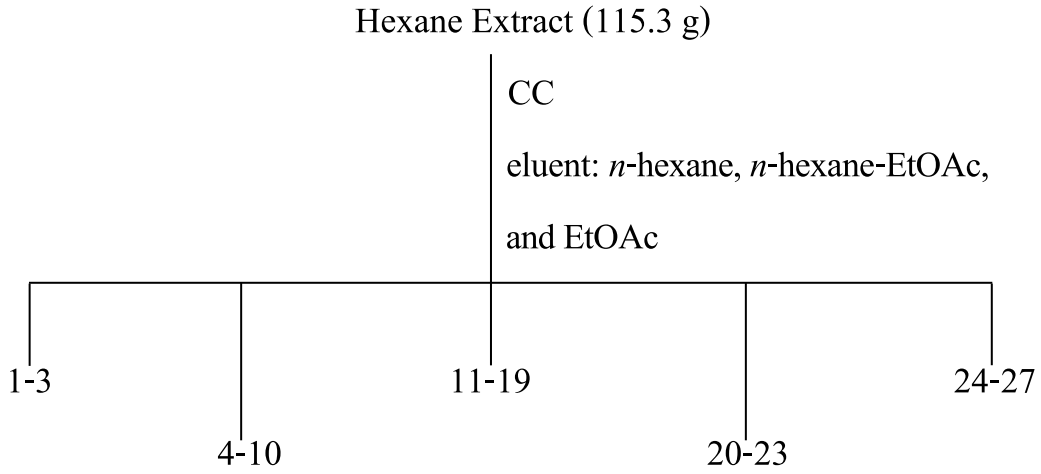
The dried stems of *D. scandens* (10.0 kg) were milled and extracted successively with *n*-hexane, EtOAc and MeOH for five times of each solvent at room temperature. The filtered solution of each extraction was evaporated to dryness under reduced pressure at temperature 40-45 °C to give the hexane extract (dark brown gum, 115.7 g), the EtOAc extract (dark brown gum, 388.8 g) and the MeOH extract (dark brown gum, 700.5 g). The extraction sequence is shown in Scheme 1.



Scheme 1 Extraction of the Stems of *D. scandens*

Hexane Extract

The hexane extract (115.3 g) was fractionated by column chromatography using a gradient solvent system of *n*-hexane, *n*-hexane-EtOAc and EtOAc with increasing amount of the more polar solvent. The elutes were examined by TLC and 5 groups of eluting fractions were obtained (see Scheme 2).



Gr. 1, Fractions 1-3 (10.0 g)

Gr. 2, Fractions 4-10 (40.7 g)

Gr. 3, Fractions 11-19 (36.0 g)

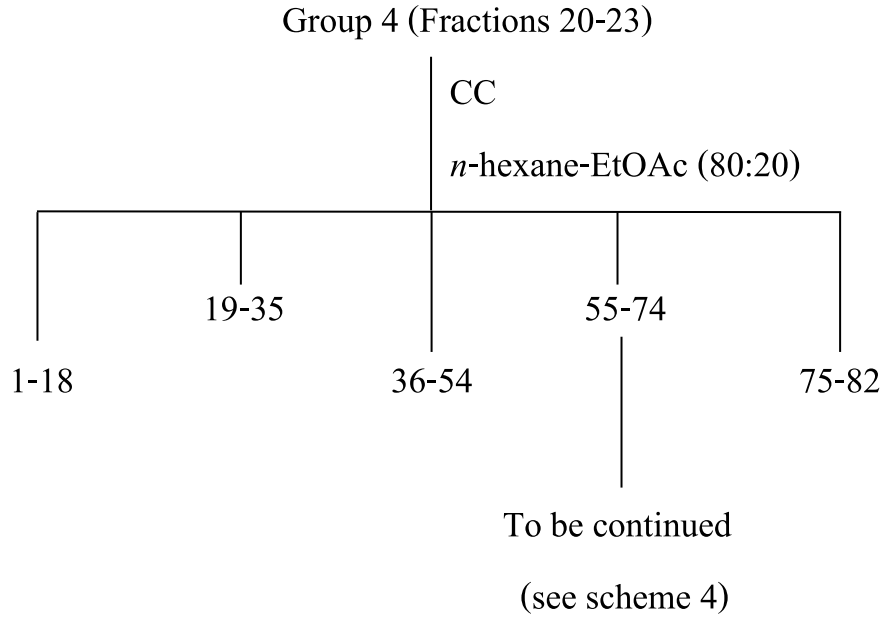
Gr. 4, Fractions 20-23 (7.0 g)

Gr. 5, Fractions 24-27 (22.0 g)

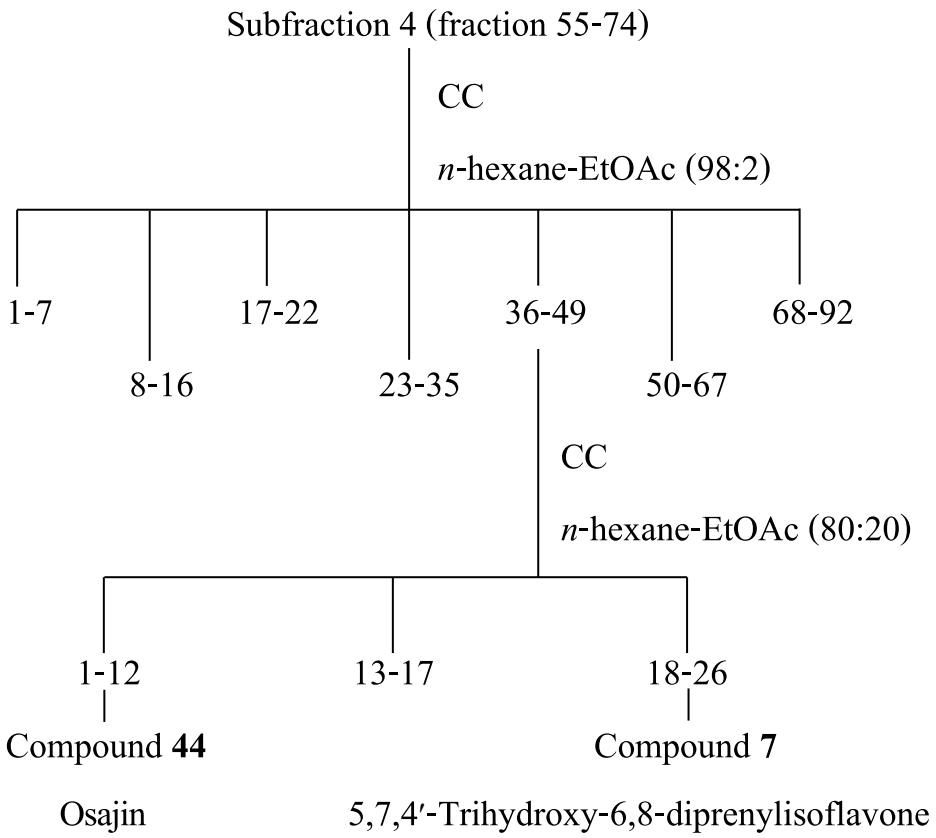
Scheme 2 Fractionation of the Hexane Extract of *D. scandens*

Group 4 (Fractions 20-23)

This combined fraction was chromatographed over silica gel eluting with *n*-hexane-EtOAc (80:20) and EtOAc to give 5 subfractions as shown in Scheme 3. Subfraction 4 (fractions 55-74) was chromatographed using *n*-hexane-EtOAc (98:2) to afford 7 subfractions. Subfraction 5 (fractions 36-49) was chromatographed using *n*-hexane-EtOAc (80:10) to yield osajin (**44**) as yellow amorphous solid (221.6 mg) and 5,7,4′-trihydroxy-6,8 diprenylisoflavone (**7**) as yellow amorphous solid (6.7 mg) as shown in Scheme 4.



Scheme 3 Fractionation of Group 4 (Fractions 20-23) of the Hexane Extract



Scheme 4 Fractionation of Subfraction 4 (Fractions 55-74) of Scheme 3

Osajin (44)

IR: ν_{max} 3414, 2973, 1642, 1617, 1572, 1513, 1432, 1358, 1238, 1169, 1074, 873 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 17.

ESIMS (-ve): *m/z* (% rel. intensity) 403 $[M–H]^-$ (100).

5,7,4′-Trihydroxy-6,8-diprenylisoflavone (7)

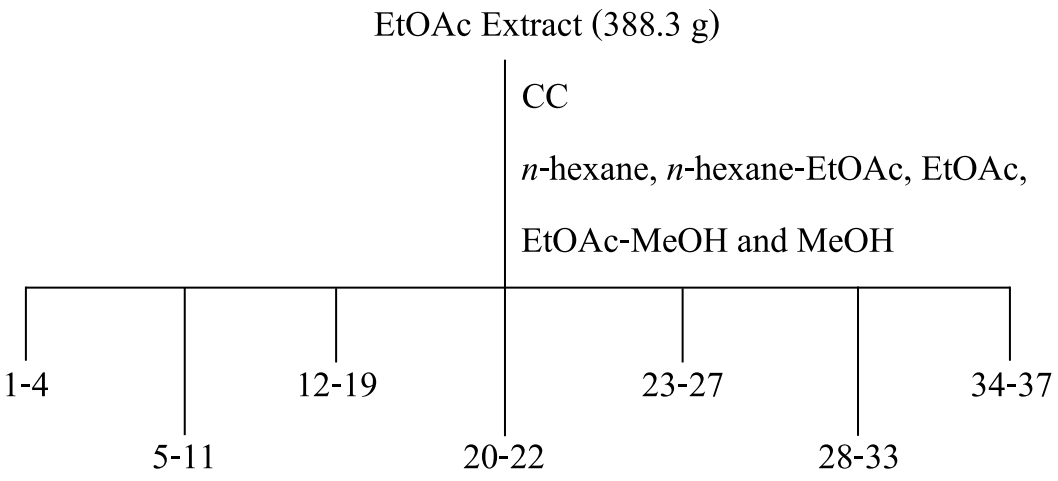
IR: ν_{max} 3347, 2919, 1643, 1611, 1557, 1514, 1429, 1334, 1267, 1202, 1171, 1078, 1065, 946, 833 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 12.

ESIMS (-ve): *m/z* (% rel. intensity) 405 $[M–H]^-$ (100).

EtOAc Extract

The EtOAc extract (388.3 g) was fractionated by column chromatography using a gradient solvent system of *n*-hexane, *n*-hexane-EtOAc, EtOAc, EtOAc-MeOH and MeOH with increasing amount of the more polar solvent. The elutes were examined by TLC and 7 combined fractions were obtained (see Scheme 5).



Gr. 1, Fractions 1-4 (19.0 g)

Gr. 2, Fractions 5-11 (30.0 g)

Gr. 3, Fractions 12-19 (157.6 g)

Gr. 4, Fractions 20-22 (24.2 g)

Gr. 5, Fractions 23-27 (30.8 g)

Gr. 6, Fractions 28-33 (84.2 g)

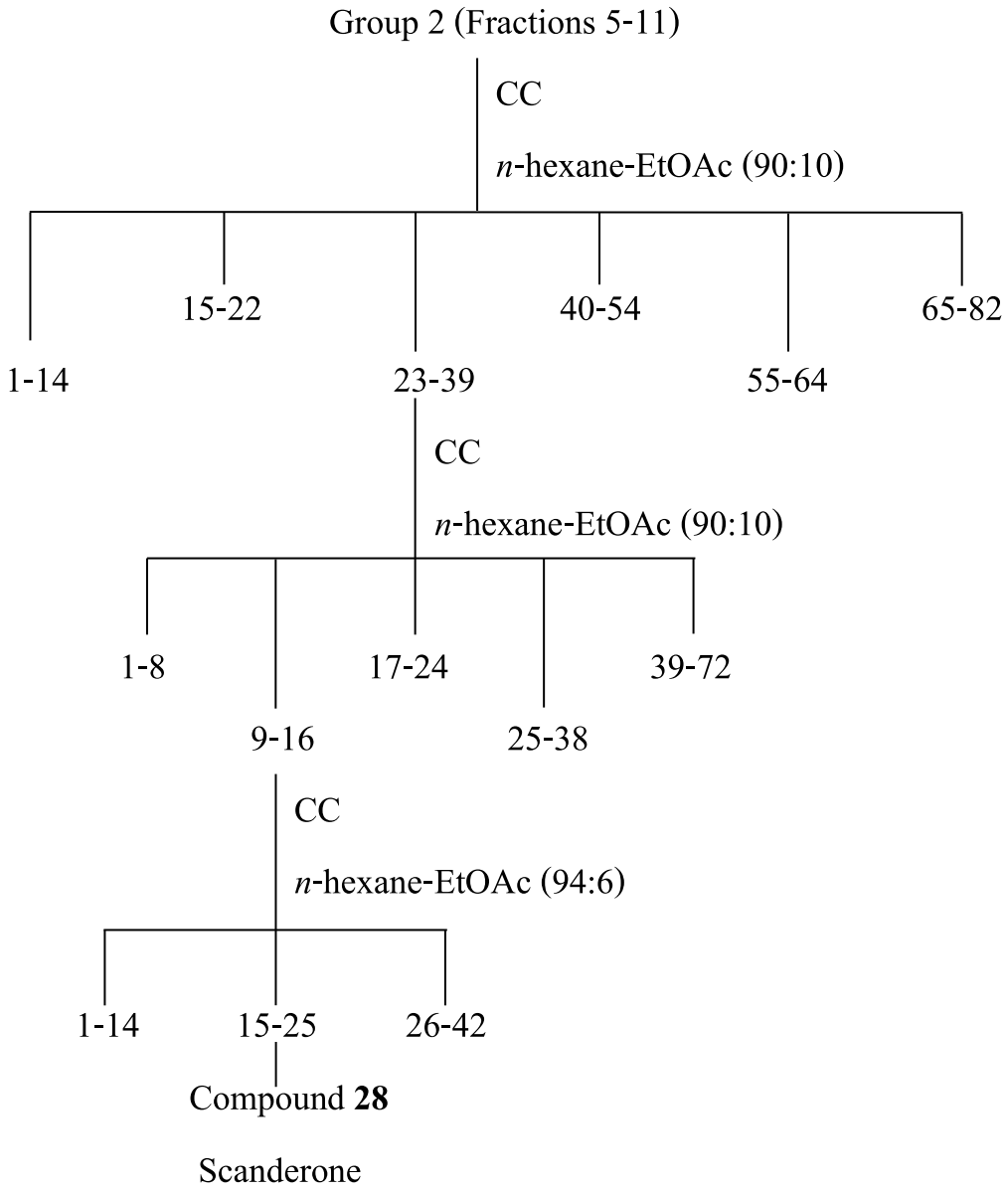
Gr. 7, Fractions 34-37 (43.0 g)

Scheme 5 Fractionation of the EtOAc Extract of *D. scandens*

Group 2 (Fractions 5-11)

This combined fraction was chromatographed over silica gel eluting with *n*-hexane-EtOAc (90:10) to give 6 subfractions. Subfraction 3 (fractions 23-39) was chromatographed using *n*-hexane-EtOAc (90:10) to afford 5 subfractions. Subfraction 2 (fractions 9-16) was chromatographed using *n*-hexane-EtOAc (94:6) as eluent to give 3 subfractions. Subfraction 2 was

identified as scanderone (**28**) as yellow amorphous solid (225.7 mg) as shown in Scheme 6.



Scheme 6 Fractionation of Group 2 (Fractions 5-11) of the EtOAc Extract

Scanderone (28)

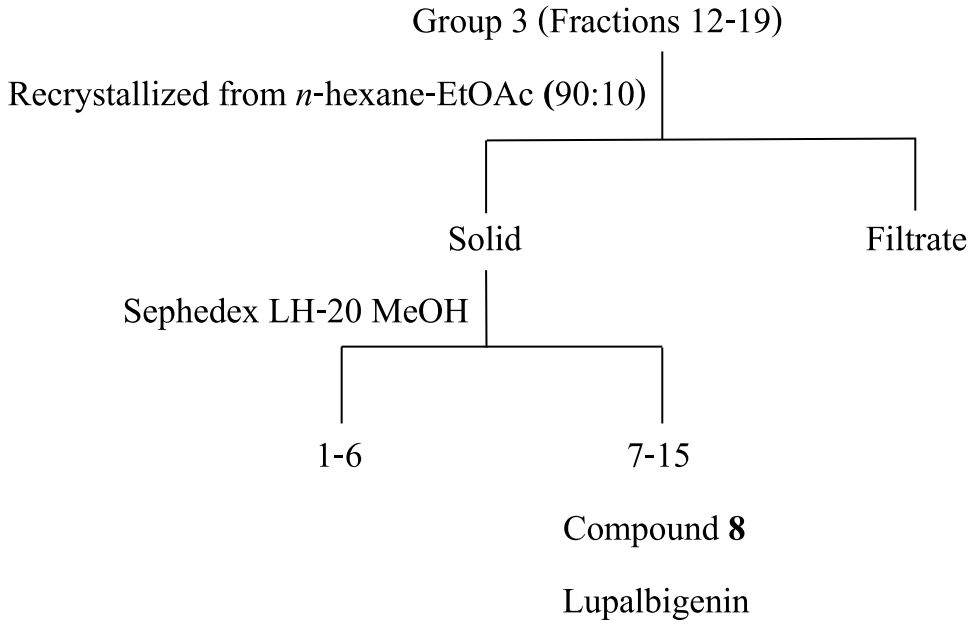
IR: ν_{max} 3333, 2974, 1649, 1617, 1570, 1456, 1270, 1248, 1213, 1059, 819 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 15.

ESIMS (-ve): *m/z* (% rel. intensity) 403 $[M–H]^-$ (100).

Group 3 (Fractions 12-19)

This combined fraction was recrystallized from *n*-hexane-EtOAc (90:10) to give a solid containing a mixture of compounds, which was separated on Sephadex LH-20 column eluting with MeOH to give 2 subfractions. Subfraction 2 was identified as lupalbigenin (**8**) as pale yellow amorphous solid (12.7 g) as shown in Scheme 7.



Scheme 7 Fractionation of Group 3 (Fractions 12-19) of the EtOAc Extract

Lupalbigenin (8)

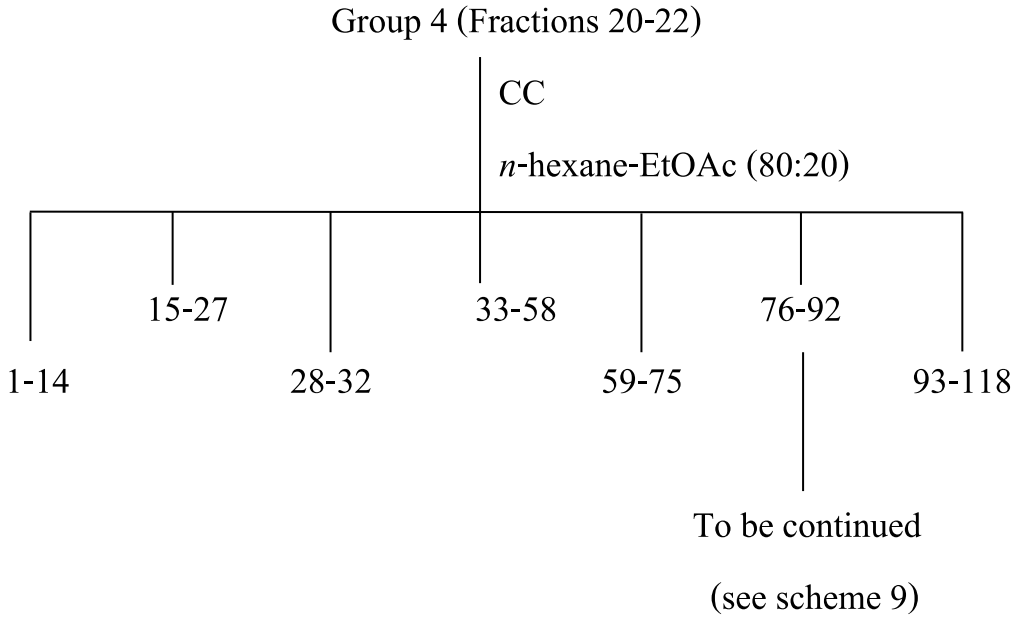
IR: ν_{max} 3244, 2924, 1652, 1618, 1559, 1502, 1462, 1427, 1304, 1271, 1118, 1174, 1069, 823 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 13.

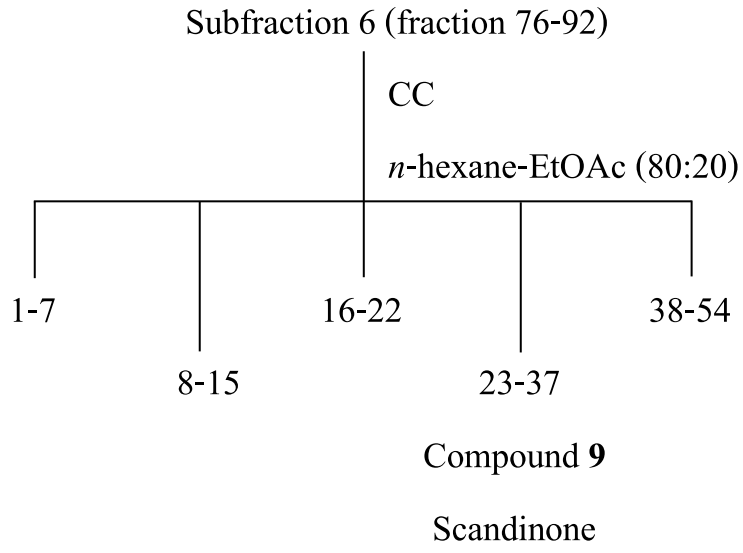
ESIMS (-ve): *m/z* (% rel. intensity) 405 $[M–H]^-$ (100).

Group 4 (Fractions 20-22)

This combined fraction was chromatographed over silica gel eluting with *n*-hexane-EtOAc (80:20) to give 7 subfractions as shown in Scheme 8. Subfraction 6 (fractions 76-92) was chromatographed using *n*-hexane-EtOAc (80:20) to give 5 subfractions. Subfraction 4 was identified as scandinone (**9**) as yellow amorphous (101.7 mg) (see Scheme 9).



Scheme 8 Fractionation of Group 4 (Fractions 20-22) of the EtOAc Extract



Scheme 9 Fractionation of Subfraction 6 (Fractions 76-79) of Scheme 8

Scandinone (9)

IR: ν_{max} 3369, 2967, 1627, 1606, 1582, 1571, 1419, 1377, 1248, 1217, 1132, 1074, 833 cm^{-1}.

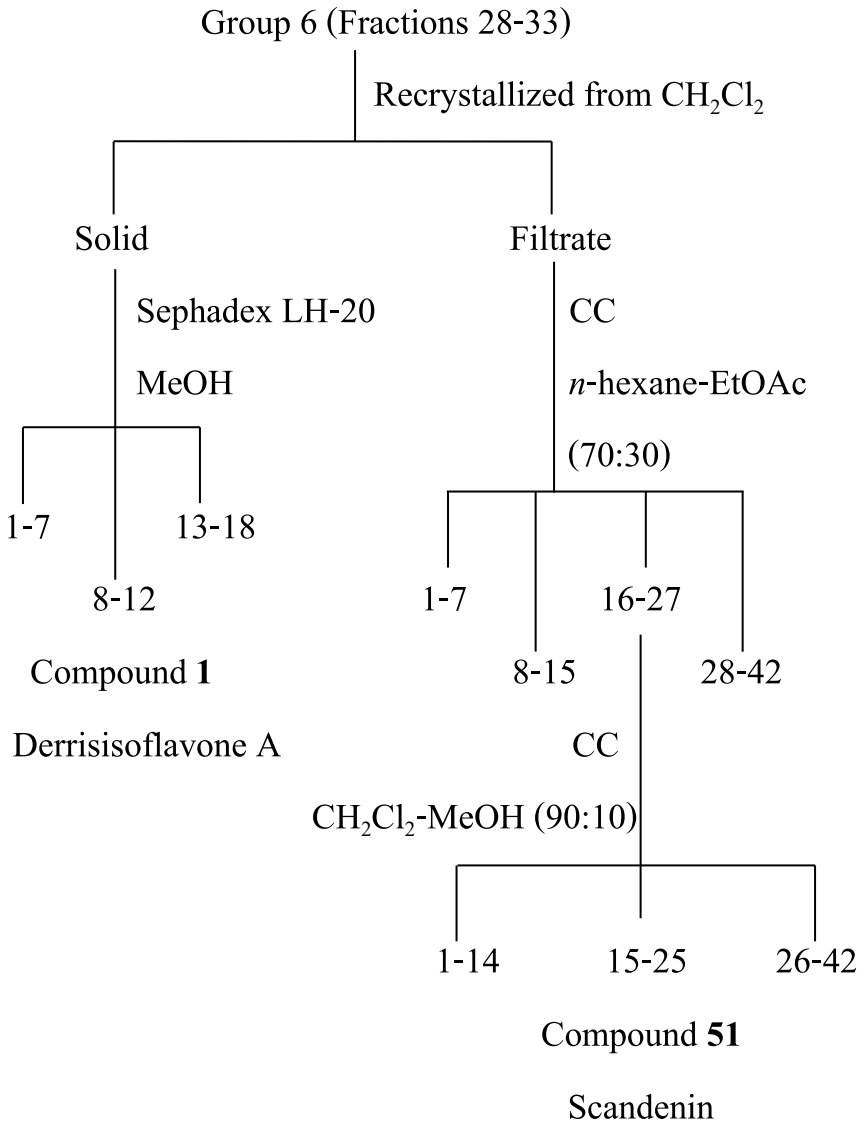
^{1}H- and ^{13}C-NMR data are given in Table 14.

ESIMS (+ve): *m/z* (% rel. intensity) 859 $[2M+Na]^{+}$ (70).

Group 6 (Fractions 28-33)

This combined fraction was recrystallized from CH_2Cl_2 to give a solid containing a mixture of compounds, which was separated on Sephadex LH-20 column eluting with MeOH to give 3 subfractions. Subfraction 3 was identified as derrisisoflavone A (**1**) as yellow amorphous solid (5.7 g). The filtrate was chromatographed over silica gel eluting with *n*-hexane-EtOAc (70:30) to give 4 subfractions. Subfraction 3 was chromatographed using 10% MeOH in CH_2Cl_2

to give 3 subfractions. Subfraction 3 was identified as scandenin (**51**) as white amorphous solid (3.2 mg) (see Scheme 10).



Scheme 10 Fractionation of Group 6 (Fractions 28-33) of the EtOAc Extract

Derrisisoflavone A (1)

IR: ν_{max} 3162, 2937, 1630, 1607, 1583, 1514, 1415, 1374, 1259, 1218, 1171, 1070, 992, 845 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 11.

ESIMS (-ve): *m/z* (% rel. intensity) 419 $[M–H]^-$ (100).

Scandenin (51)

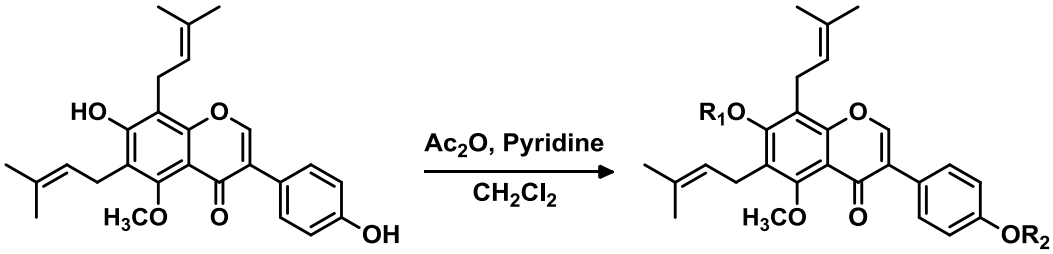
IR: ν_{max} 3216, 2922, 1679, 1614, 1588, 1517, 1424, 1375, 1274, 1220, 1173, 1115, 998, 832 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 18.

ESIMS (-ve): *m/z* (% rel. intensity) 433 $[M–H]^-$ (100).

Structural Modification

Acetylation of Derrisisofleavone A (1)



(**1**) (**124-126**)

124; R_1 = Ac, R_2 = H

125; R_1 = H, R_2 = Ac

126; R_1 = R_2 = Ac

Derrisisoflavone A (**1**) (100.0 mg, 0.24 mmol) was dissolved in CH_2Cl_2 (12.5 ml) and pyridine (5 ml) and acetic anhydride (46 µl) was then added. The mixture was stirred at room temperature for 4 h. Water was added and the mixture was extracted with CH_2Cl_2 (3x75 ml). The combined organic phase was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude mixture was purified by silica column chromatography eluting with *n*-hexane-EtOAc (85:15) to give the acetates **124** (15.9 mg, 14%), **125** (4.0 mg, 3%) and **126** (52.7 mg, 44%).

Derrisisoflavone A 7-*O*-acetate (124)

IR: ν_{max} 3176, 2923, 1767, 1625, 1610, 1584, 1515, 1415, 1363, 1268, 1192, 1174, 1054, 832 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 19.

HR-TOFMS (ESI^{+}): *m/z* 485.1931 $[M+Na]^{+}$ (Calcd. for $C_{28}H_{30}O_{6}$+Na, 485.1935).

Derrisisoflavone A 4′-*O*-acetate (125)

IR: ν_{max} 3319, 2926, 1760, 1633, 1585, 1506, 1417, 1369, 1265, 1195, 1166, 1066, 1063, 843 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 19.

HR-TOFMS (ESI^{+}): *m/z* 485.1933 $[M+Na]^{+}$ (Calcd. for $C_{28}H_{30}O_{6}$+Na, 485.1935).

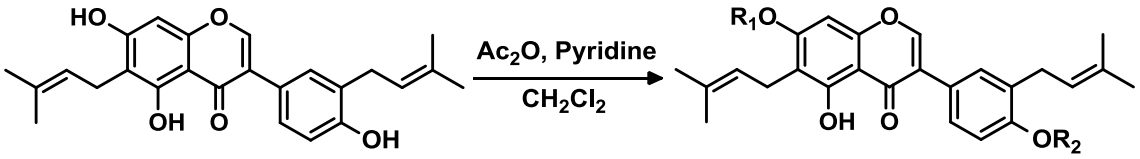
Derrisisoflavone A 7,4′-di-*O*-acetate (126)

IR: ν_{max} 2975, 2917, 1766, 1754, 1644, 1586, 1509, 1447, 1415, 1365, 1269, 1193, 1169, 1114, 1072, 1063, 857 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 20.

HR-TOFMS (ESI^{+}): *m/z* 527.2039 $[M+Na]^{+}$ (Calcd. for $C_{30}H_{32}O_{7}$+Na, 527.2040).

Acetylation of Lupalbigenin (8)



(**8**) (**127-129**)

127; R_1 = Ac, R_2 = H

128; R_1 = H, R_2 = Ac

129; R_1 = R_2 = Ac

Lupalbigenin (**8**) (100 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (25 ml), pyridine (0.1 ml) and acetic anhydride (24 µl) was added. The mixture was stirred at room temperature for 4 h. Water was added and the mixture was extracted with CH_2Cl_2 (3x75 ml). The combined organic phase was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude mixture was purified by silica column chromatography eluting with *n*-hexane-EtOAc (75:15) to give the acetates **127** (35.9 mg, 33%), **128** (10.9 mg, 10%) and **129** (68.5 mg, 57%).

Lupalbigenin 7-*O*-acetate (127)

IR: ν_{max} 3488, 2914, 1734, 1621, 1592, 1507, 1440, 1266, 1206, 1170, 1058, 837 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 21.

HR-TOFMS (ESI^{+}): *m/z* 471.1776 $[M+Na]^{+}$ (Calcd. for $C_{27}H_{28}O_{6}$+Na, 471.1778).

Lupalbigenin 4′-*O*-acetate (128)

IR: ν_{max} 3193, 2917, 1733, 1642, 1618, 1494, 1433, 1294, 1225, 1167, 1100, 1057, 810 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 21.

HR-TOFMS (ESI^{+}): *m/z* 471.1767 $[M+Na]^{+}$ (Calcd. for $C_{27}H_{28}O_{6}$+Na, 471.1778).

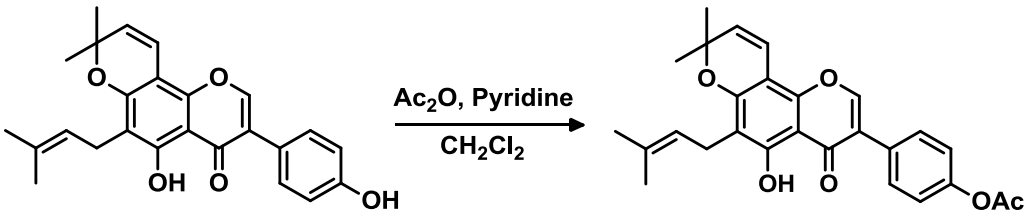
Lupalbigenin 7,4′-di-*O*-acetate (129)

IR: ν_{max} 3081, 2912, 1748, 1626, 1593, 1439, 1367, 1205, 1165, 1120, 1085, 1059, 904, 841 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 22.

HR-TOFMS (ESI^{+}): *m/z* 513.1879 $[M+Na]^{+}$ (Calcd. for $C_{29}H_{30}O_{7}$+Na, 513.1884).

Acetylation of Osajin (44)



(**44**) (**130**)

Osajin (**44**) (25 mg, 0.06 mmol) was dissolved in CH_2Cl_2 (7.5 ml), pyridine (0.5 ml) and acetic anhydride (10 µl) was added. The mixture was stirred at room temperature for 24 h. Water was added and the mixture was extracted with CH_2Cl_2 (3x75 ml). The combined organic phase was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude mixture was purified by Sephadex LH-20 eluting with 30% CH_2Cl_2 in MeOH to give the acetate **130** (25.4 mg, 95%).

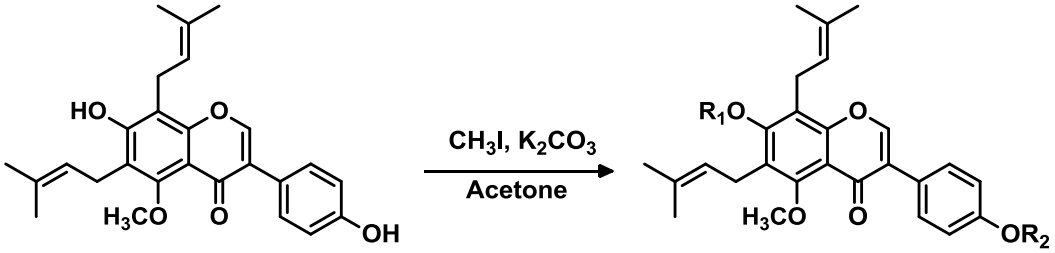
Osajin 4′-*O*-acetate (130)

IR: ν_{max} 3341, 2981, 2924, 1750, 1651, 1615, 1573, 1508, 1433, 1360, 1241, 1208, 1169, 1116, 1073, 843 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 23.

HR-TOFMS (ESI^{+}): *m/z* 469.1633 $[M+Na]^{+}$ (Calcd. for $C_{27}H_{26}O_6$+Na, 469.1622).

Methylation of Derrisisoflavone A (1)



(**1**) (**131-133**)

131; $R_1 = CH_3$, $R_2 = H$

132; $R_1 = H$, $R_2 = CH_3$

133; $R_1 = R_2 = CH_3$

Derrisisoflavone A (**1**) (100 mg, 0.24 mmol) was dissolved in acetone (20 ml) and methyl iodide (1 ml) was added. The mixture was stirred at 40 ^{o}C for 4 h. Water was added and the mixture was extracted with CH_2Cl_2 (3x75 ml). The combined organic phase was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude mixture was purified by silica column chromatography eluting with *n*-hexane-EtOAc (80:10) to give the methyl ethers **131** (35.6 mg, 34%), **132** (18.4 mg, 18%) and **133** (20.6 mg, 19%).

Derrissioflavone A 7-*O*-methyl ether (131)

IR: ν_{max} 3362, 2925, 1634, 1608, 1587, 1516, 1420, 1375, 1260, 1215, 1174, 1122, 1070, 993, 833 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 24.

HR-TOFMS (ESI^{+}): *m/z* 457.1959 $[M+Na]^{+}$ (Calcd. for $C_{27}H_{30}O_5$+Na, 457.1985).

Derrissioflavone A 4′-*O*-methyl ether (132)

IR: ν_{max} 3344, 2922, 1633, 1607, 1587, 1512, 1464, 1418, 1374, 1291, 1246, 1220, 1177, 1075, 1031, 832 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 24.

HR-TOFMS (ESI^{+}): *m/z* 457.1961 $[M+Na]^{+}$ (Calcd. for $C_{27}H_{30}O_5$+Na, 457.1985).

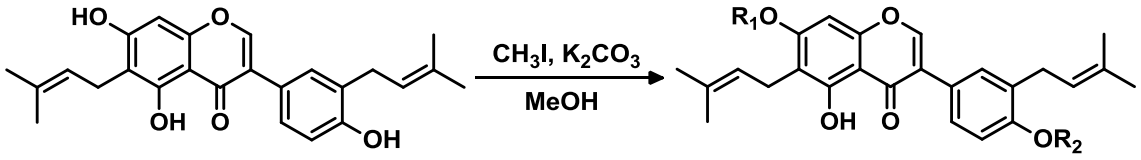
Derrissioflavone A 7,4′-di-*O*-methyl ether (133)

IR: ν_{max} 2938, 1638, 1608, 1582, 1512, 1420, 1248, 1220, 1177, 1074, 1029, 832 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 25.

HR-TOFMS (ESI^{+}): *m/z* 471.2113 $[M+Na]^{+}$ (Calcd. for $C_{28}H_{32}O_5$+Na, 471.2142).

Methylation of Lupalbigenin (8)



(**8**) (**134-135**)

134; $R_1 = CH_3$, $R_2 = H$

135; $R_1 = R_2 = CH_3$

Lupalbigenin (**8**) (100 mg, 0.24 mmol) was dissolved in methanol (3 ml) and methyl iodide (5 ml) was added. The mixture was stirred at 40 ^{o}C for 4 h. Water was added and the mixture was extracted with CH_2Cl_2 (3x75 ml). The combined organic phase was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude mixture was purified by silica column chromatography eluting with *n*-hexane-EtOAc (93:7) to give the methyl ethers **134** (71.6 mg, 71%) and **135** (26.7 mg, 26%).

Lupalbigenin 7-*O*-methyl ether (134)

IR: ν_{max} 3326, 2921, 1649, 1613, 1573, 1491, 1447, 1265, 1219, 1171, 1116, 1057, 818 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 26.

HR-TOFMS (ESI^{+}): *m/z* 443.1808 $[M+Na]^{+}$ (Calcd. for $C_{26}H_{28}O_5$+Na, 443.1829).

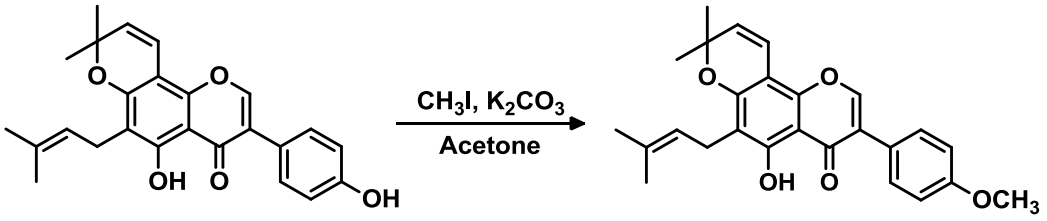
Lupalbigenin 7,4′-di-*O*-methyl ether (135)

IR: ν_{max} 3347, 2968, 2919, 1644, 1608, 1568, 1501, 1449, 1264, 1222, 1122, 1078, 1057, 819 cm^{-1}

^{1}H- and ^{13}C-NMR data are given in Table 26.

HR-TOFMS (ESI^{+}): *m/z* 457.1983 $[M+Na]^{+}$ (Calcd. for $C_{27}H_{30}O_5$+Na, 457.1985).

Methylation of Osajin (44)



(**44**) (**43**)

Osajin (**44**) (30 mg, 0.07 mmol) was dissolved in acetone (15 ml) and methyl iodide (1 ml) was added. The mixture was stirred at 40 ^{o}C for 24 h. Water was added and the mixture was extracted with CH_2Cl_2 (3x75 ml). The combined organic phase was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude mixture was purified by silica column chromatography eluting with *n*-hexane-EtOAc (96:4) to give the methyl ether **43** (26.2 mg, 84%).

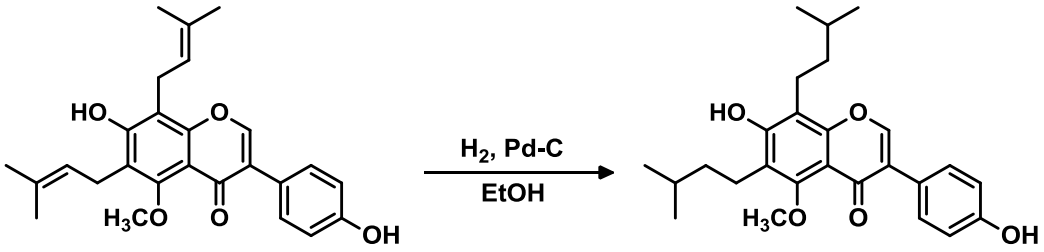
4′-*O*-Methylosajin (43)

IR: ν_{max} 3321, 2979, 2911, 1650, 1614, 1567, 1510, 1434, 1243, 1206, 1175, 1147, 1119, 1077, 830 cm^{-1}

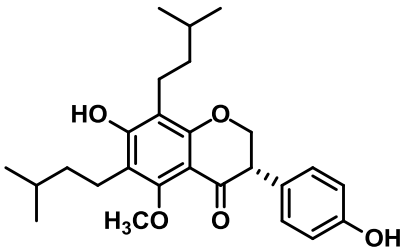
^{1}H- and ^{13}C-NMR data are given in Table 16.

HR-TOFMS (ESI^{+}): *m/z* 441.1645 $[M+Na]^{+}$ (Calcd. for $C_{26}H_{26}O_5$+Na, 441.1672).

Catalytic Hydrogenation of Derrisisoflavone A (1)



(**1**) (**136**)



(**137**)

Derrisisoflavone A (**1**) (100 mg, 0.24 mmol) in ethanol (2 ml) was hydrogenated at atmospheric pressure, with 10% Pd-C as a catalyst. The reaction was filtered through a short Celite column and the residue was washed with MeOH. The filtered solution was evaporated to dryness. The crude mixture was purified by silica column chromatography eluting with *n*-

hexane-EtOAc (85:15) to give the tetrahydro analogue **136** (48.9 mg, 49%) and hexahydro analogue **137** (45.6 mg, 45%).

Tetrahydroderrisisoflavone A (136)

IR: ν_{max} 3173, 2953, 1631, 1607, 1586, 1516, 1466, 1416, 1220, 1187, 1137, 1077, 845 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 27.

HR-TOFMS (ESI^{+}): *m/z* 447.2145 $[M+Na]^{+}$ (Calcd. for $C_{26}H_{32}O_5$+Na, 447.2142).

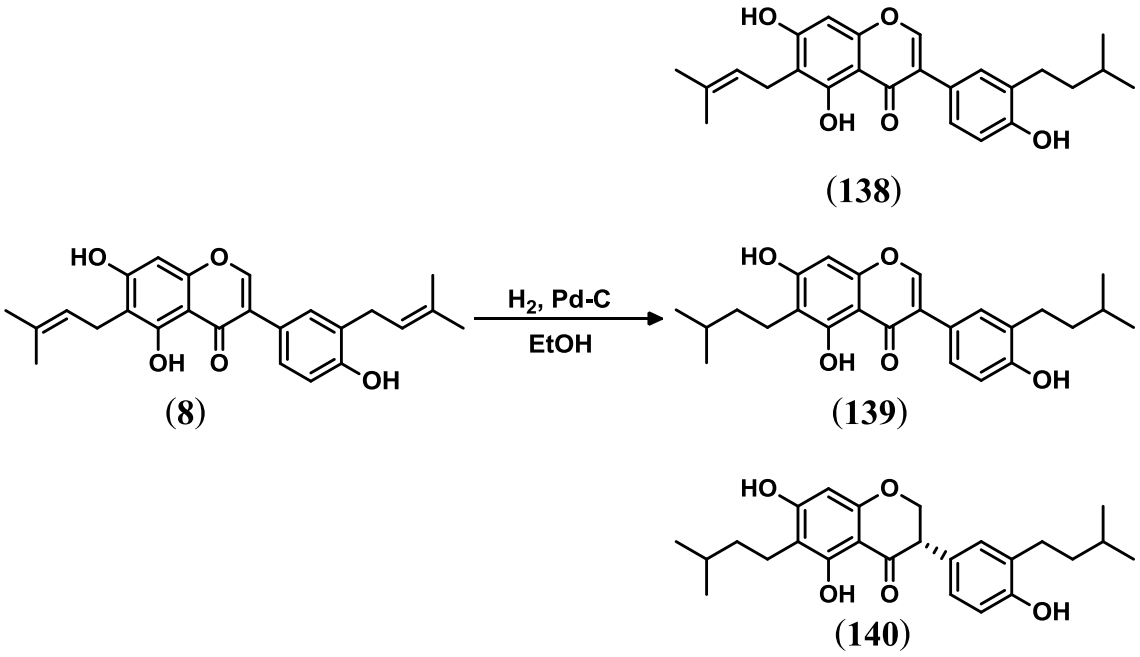
Hexahydroderrisisoflavone A (137)

IR: ν_{max} 3339, 2955, 2869, 1581, 1517, 1467, 1385, 1209, 1159, 1116, 1001, 831 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 27.

HR-TOFMS (ESI^{+}): *m/z* 449.2294 $[M+Na]^{+}$ (Calcd. for $C_{26}H_{34}O_5$+Na, 449.2298).

Catalytic Hydrogenation of Lupalbigenin (8)



Lupalbigenin (**8**) (100 mg, 0.24 mmol) in ethanol (2ml) was hydrogenated at atmospheric pressure, with 10% Pd-C as a catalyst. The reaction was filtered through a short Celite column and the residue was washed with MeOH. The filtered solution was evaporated to dryness. The crude mixture was purified by silica column chromatography eluting *n*-hexane-EtOAc (90:10) to give the dihydro analogue **138** (8.8 mg, 9%), tetrahydro analogue **139** (46.3 mg, 47%) and hexahydro analogue **140** (24.8 mg, 26%).

Dihydrolupalbigenin (138)

IR: ν_{max} 3263, 2963, 2915, 1651, 1616, 1552, 1506, 1466, 1420, 1231, 1219, 1173, 1127, 1055, 812 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 28.

HR-TOFMS (ESI^{+}): *m/z* 431.1829 $[M+Na]^{+}$ (Calcd. for $C_{32}H_{36}O_{7}$+Na, 431.1829).

Tetrahydrolupalbigenin (139)

IR: ν_{max} 3261, 2954, 2923, 1651, 1620, 1609, 1560, 1466, 1422, 1350, 1229, 1124, 1053, 817 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 28.

HR-TOFMS (ESI^{+}): *m/z* 433.1947 $[M+Na]^{+}$ (Calcd. for $C_{25}H_{30}O_{5}$+Na, 433.1985).

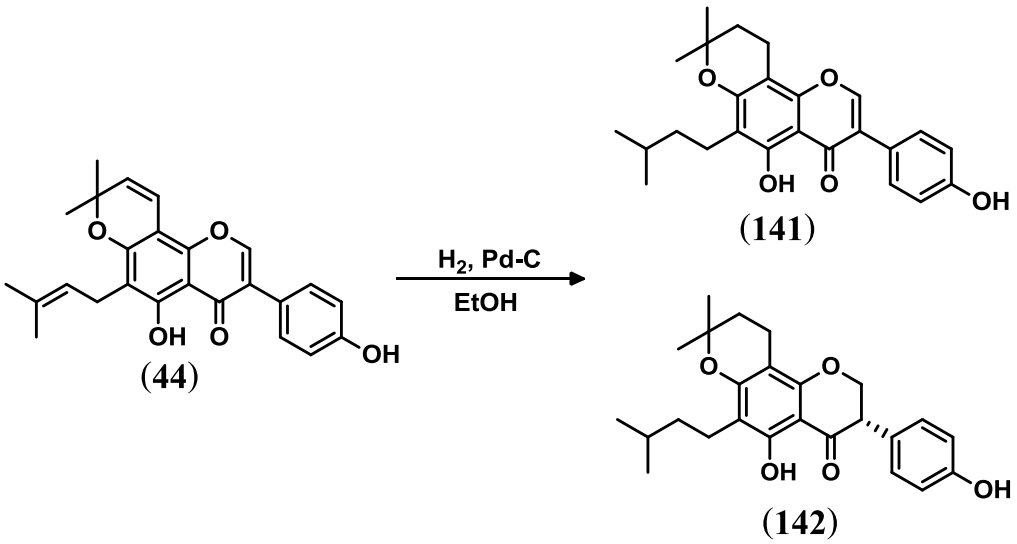
Hexahydrolupalbigenin (140)

IR: ν_{max} 3254, 2958, 2913, 1616, 1551, 1504, 1466, 1420, 1358, 1275, 1254, 1173, 1127, 1055, 812 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 29.

HR-TOFMS (ESI^{+}): *m/z* 435.2145 $[M+Na]^{+}$ (Calcd. for $C_{25}H_{32}O_{5}$+Na, 435.2142).

Catalytic Hydrogenation of Osajin (44)



Osajin (**44**) (50 mg, 0.12 mmol) in ethanol (2 ml) was hydrogenated at atmospheric pressure, with 10% Pd-C as a catalyst. The reaction was filtered through a short Celite column and the residue was washed with MeOH. The filtered solution was evaporated to dryness. The crude mixture was purified by sephadex-LH20 eluting with MeOH to give the tetrahydro analogue **141** (23.1 mg, 46%) and hexahydro analogue **142** (21.0 mg, 41%).

Tetrahydroosajin (141)

IR: ν_{max} 3375, 2936, 1643, 1611, 1569, 1515, 1428, 1367, 1284, 1207, 1160, 1114, 1070, 811 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 30.

HR-TOFMS (ESI^{+}): *m/z* 431.1798 $[M+Na]^{+}$ (Calcd. for $C_{25}H_{28}O_5$+Na, 431.1829).

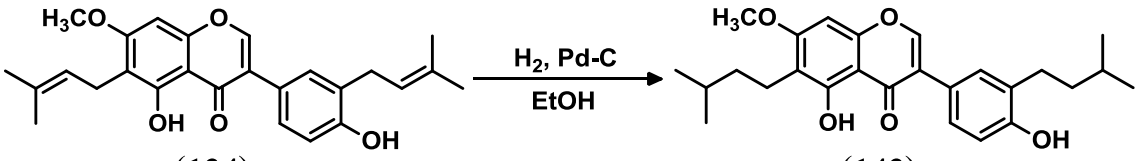
Hexahydroosajin (142)

IR: ν_{max} 3431, 2942, 1604, 1589, 1519, 1435, 1384, 1267, 1202, 1169, 1120, 833 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 30.

HR-TOFMS (ESI^{+}): *m/z* 433.1983 $[M+Na]^{+}$ (Calcd. for $C_{25}H_{30}O_5$+Na, 433.1985).

Catalytic Hydrogenation of Lupalbigenin 7-*O*-methyl ether (134)



(**134**) (**143**)

Lupalbigenin 7-*O*-methyl ether (**134**) (50 mg, 0.12 mmol) was dissolved in ethanol (2 ml) was hydrogenated at atmospheric pressure, with 10% Pd-C as a catalyst. The reaction was filtered through a short celite column and the residue was washed with MeOH. The filtered solution was evaporated to dryness. The crude mixture was purified by silica column chromatography eluting *n*-hexane-EtOAc (90:10) to give the tetrahydro analogue **143** (15 mg, 29%).

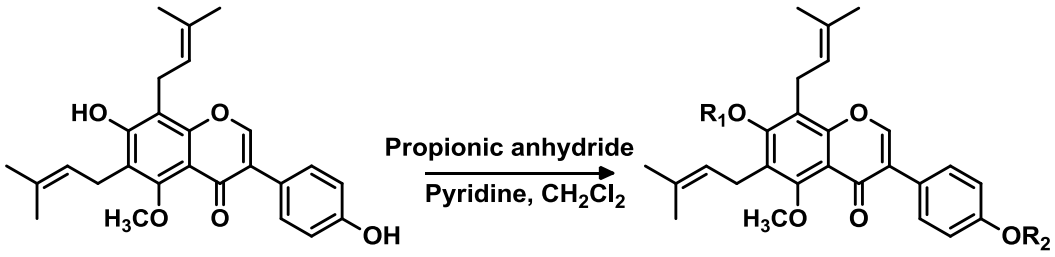
Tetrahydrolupalbigenin 7-*O*-methyl ether (143)

IR: ν_{max} 3382, 2953, 1649, 1614, 1572, 1506, 1448, 1361, 1272, 1222, 1141, 1069, 1054, 819 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 31.

HR-TOFMS (ESI^{+}): *m/z* 447.2138 $[M+Na]^{+}$ (Calcd. For $C_{26}H_{32}O_5$+Na, 447.2141).

Esterification of Derrisisofleavone A (1) with Propionic anhydride



(**1**) (**144-146**)

144; $R_1 = COCH_2CH_3$, $R_2 = H$

145; $R_1 = H$, $R_2 = COCH_2CH_3$

146; $R_1 = R_2 = COCH_2CH_3$

Derrisisoflavone A (**1**) (100 mg, 0.24 mmol) was dissolved in dichloromethane (12.5 ml) and pyridine (5 ml) and propionic anhydride (46 µl) was then added. The mixture was stirred at room temperature for 4 h. Water was added and the mixture was extracted with CH_2Cl_2. The combined organic phase was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude mixture was purified by silica

column chromatography eluting with 10% EtOAc in *n*-hexane to give the propanoates **144** (15.9 mg, 14%), **145** (4.0 mg, 3%) and **146** (52.7 mg, 44%).

Derrisisoflavone A 7-*O*-propanoate (144)

IR: ν_{max} 3350, 2926, 1758, 1630, 1587, 1512, 1414, 1359, 1270, 1260, 1168, 1117, 1074, 835 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 32.

HR-TOFMS (ESI^{+}): *m/z* 499.2086 $[M+Na]^{+}$ (Calcd. for $C_{29}H_{32}O_{6}$+Na, 499.2091).

Derrisisoflavone A 4′-*O*-propanoate (145)

IR: ν_{max} 3316, 2928, 1758, 1631, 1583, 1505, 1415, 1372, 1265, 1230, 1166, 1137, 1072, 1060, 838 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 32.

HR-TOFMS (ESI^{+}): *m/z* 499.2090 $[M+Na]^{+}$ (Calcd. for $C_{29}H_{32}O_{6}$+Na, 499.2091).

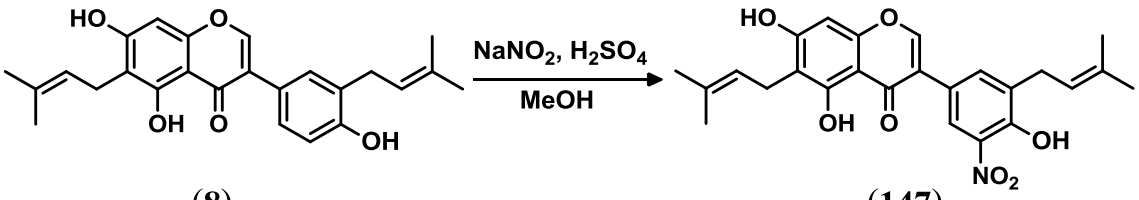
Derrisisoflavone A 7,4′-di-*O*-propanoate (146)

IR: ν_{max} 2925, 1766, 1746, 1644, 1588, 1418, 1355, 1262, 1217, 1172, 1118, 1073, 891 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 33.

HR-TOFMS (ESI^{+}): *m/z* 555.2357 $[M+Na]^{+}$ (Calcd. for $C_{32}H_{36}O_{7}$+Na, 555.2353).

Nitration of Lupalbigenin (8)



(**8**) (**147**)

Lupalbigenin (**8**) (100 mg, 0.24 mmol) was dissolved in methanol (1ml) and sodium nitrite (85 mg, excess) and conc. sulfuric acid (2 drops) were added. The mixture was stirred at room temperature for 2 days. Water was added and the mixture was extracted with EtOAc (3x75 ml). The combined organic phase was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude mixture was purified by silica column chromatography eluting with *n*-hexane-EtOAc (90:10) to give the nitro analogue **147** (24.1 mg, 22%).

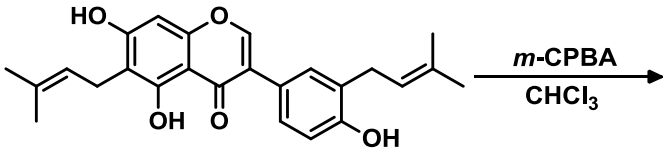
5′-Nitrolupalbigenin (147)

IR: ν_{max} 3355, 2980, 2915, 1644, 1623, 1571, 1544, 1461, 1367, 1283, 1227, 1173, 1058, 818 cm^{-1}.

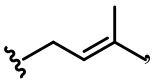
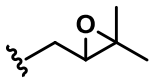
^{1}H- and ^{13}C-NMR data are given in Table 34.

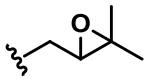
HR-TOFMS (ESI^{+}): *m/z* 474.1485 $[M+Na]^{+}$ (Calcd. for $C_{25}H_{25}NO_7$+Na, 474.1523).

Epoxidation of Lupalbigenin (8)



(**8**) (**148-149**)

148; R_1 =  R_2 = 

149; $R_1 = R_2$ = 

Lupalbigenin (**8**) (70 mg, 0.17 mmol) was dissolved in $CHCl_3$ (5ml) and *m*-chloroperbenzoic acid (*m*-CPBA) (830 mg, excess) were added. The mixture was stirred at room temperature for 3 days. 5% aq. $NaHCO_3$ was added and the mixture was extracted with EtOAc (3x75 ml). The combined organic phase was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude mixture was subjected to column chromatography using *n*-hexane-EtOAc (70:30) as eluting solvent to give the products **148** (3.5 mg, 5%) and **149** (8.9 mg, 13%).

2‴,3‴-Epoxylupalbigenin (148)

IR: ν_{max} 3242, 2978, 2923, 1645, 1614, 1578, 1497, 1453, 1297, 1264, 1221, 1142, 1119, 1059, 821 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 35.

HR-TOFMS (ESI^{+}): *m/z* 445.1618 $[M+Na]^{+}$ (Calcd. for $C_{25}H_{26}O_6$+Na, 445.1622).

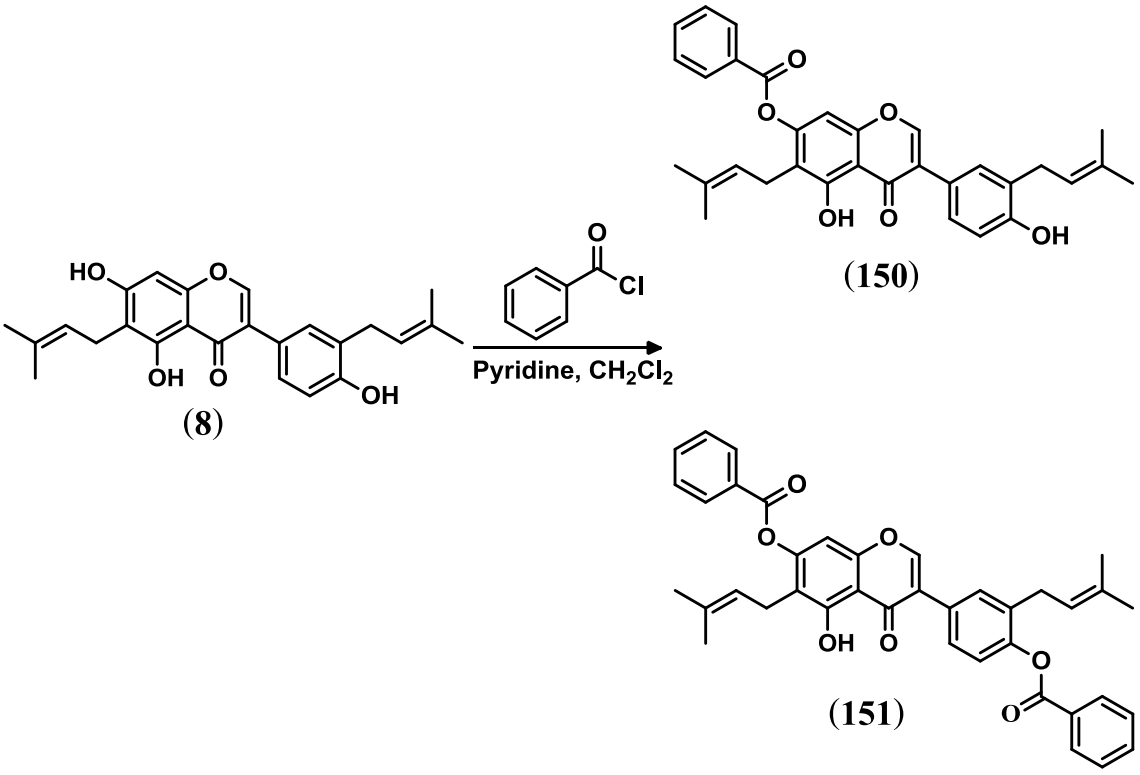
2″, 3″,2‴,3‴-Diepoxylupalbigenin (149)

IR: ν_{max} 3389, 2984, 1651, 1614, 1567, 1495, 1457, 1243, 1222, 1125, 1067, 1054, 819 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 35.

HR-TOFMS (ESI^{+}): *m/z* 461.1575 $[M+Na]^{+}$ (Calcd. for $C_{25}H_{26}O_7$+Na, 461.1571).

Benzoylation of Lupalbigenin (8)



To a solution of lupalbigenin (**8**) (50 mg, 0.12 mmol) in pyridine (2 ml) and CH_2Cl_2 (16 ml) was added benzoyl chloride (6 drops, excess). The mixture was stirred at room temperature for 4 h. Water (20 ml) was added and the mixture was extracted with EtOAc (3x75 ml). The combined organic

phase was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude mixture was purified by silica column chromatography eluting with *n*-hexane-EtOAc (90:10) to give the benzoates **150** (6.3 mg, 7%) and **151** (39.3 mg, 52%).

Lupalbigenin 7-*O*-benzoate (150)

IR: ν_{max} 3452, 2923, 1717, 1641, 1617, 1578, 1509, 1437, 1275, 1260, 1214, 1170, 1059, 826 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 36.

HR-TOFMS (ESI^{+}): *m/z* 533.1941 $[M+Na]^{+}$ (Calcd. for $C_{32}H_{30}O_6$+Na, 533.1935).

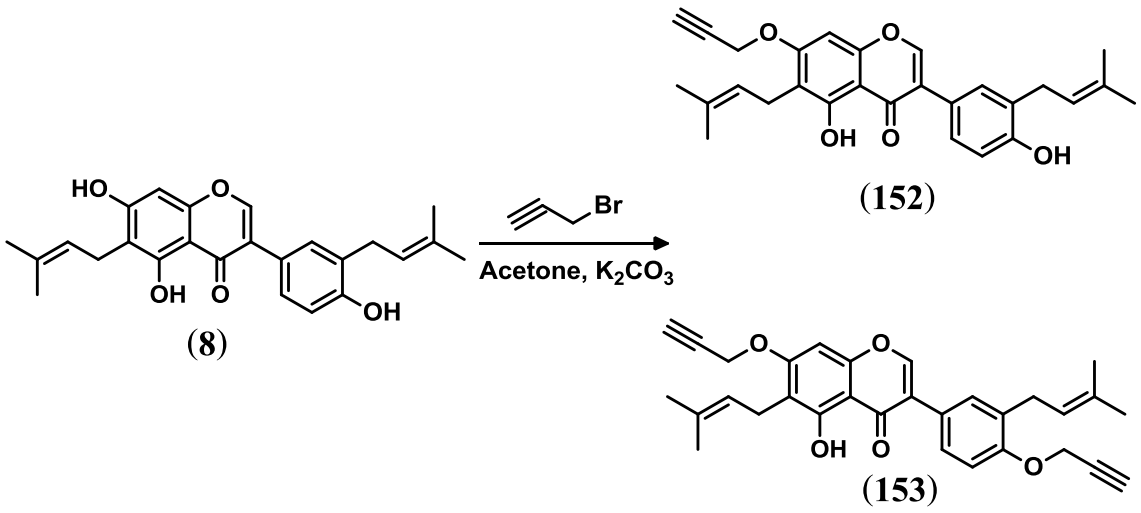
Lupalbigenin 7,4′-di-*O*-benzoate (151)

IR: ν_{max} 3062, 2975, 1750, 1733, 1645, 1619, 1582, 1512, 1447, 1245, 1223, 1165, 1106, 1058, 836, 710 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 36.

HR-TOFMS (ESI^{+}): *m/z* 637.2205 $[M+Na]^{+}$ (Calcd. for $C_{39}H_{34}O_7$+Na, 637.2197).

Reaction of Lupalbigenin (8) with Propargyl bromide



Lupalbigenin (**8**) (300 mg, 0.74 mmol) was dissolved in acetone (15 ml) and potassium carbonate (450 mg, 3.26 mmol) and propargyl bromide (1.11 ml) were then added. The mixture was stirred at room temperature for 8 h. Water was added and the mixture was extracted with CH_2Cl_2 (3x75 ml). The combined organic phase was washed with water, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude mixture was purified by silica column chromatography eluting with *n*-hexane-EtOAc (92:8) to give the propargyl ethers **152** (238.5 mg, 72%) and **153** (74.9 mg, 21%).

7-*O*-Propargyllupalbigenin (152)

IR: ν_{max} 3284, 2919, 2126, 1647, 1614, 1493, 1447, 1267, 1215, 1171, 1110, 1060, 819 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 37.

HR-TOFMS (ESI^{+}): *m/z* 467.1779 $[M+Na]^{+}$ (Calcd. for $C_{28}H_{28}O_5$+Na, 467.1829).

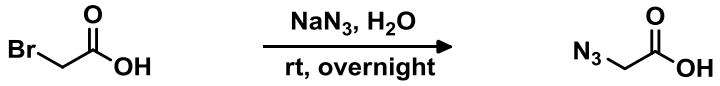
7,4′-Di-*O*-propargyllupalbigenin (153)

IR: ν_{max} 3292, 2912, 2124, 1647, 1618, 1582, 1498, 1448, 1266, 1218, 1171, 1114, 1077, 1023 818 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 37.

HR-TOFMS (ESI^{+}): *m/z* 505.1914 $[M+Na]^{+}$ (Calcd. For $C_{31}H_{30}O_5$+Na, 505.1985).

Synthesis of 2-Azidoacetic acid (154)



Bromoacetic acid (**154**)

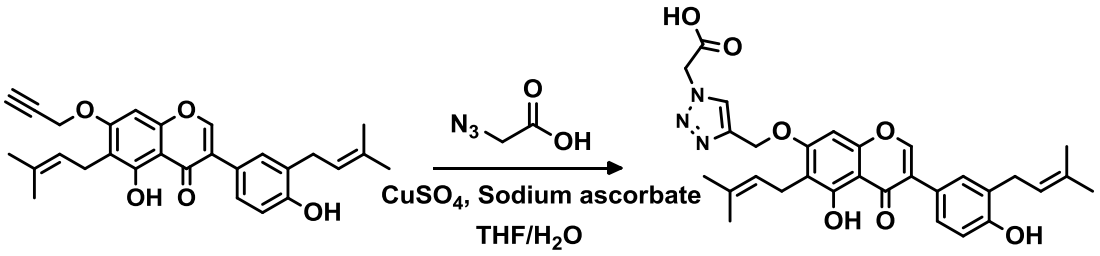
To a solution of sodium azide (2.01 g, 30.92 mmol) in cold water (20 ml) was slowly added bromoacetic acid (1.80 g, 12.95 mmol) in water (5 ml) and the mixture was allowed to stir at ambient temperature overnight. The reaction mixture was acidified to pH 1 with 3M HCl and extracted with EtOAc (3x100 ml). The organic layer was dried over anhydrous Na_2SO_4 and

the solvent was evaporated in *vacuo* to afford 2-azidoacetic acid (**154**) (1.2 g, 94%) as a colorless liquid. This compound was used in subsequent reaction.

2-Azidoacetic acid (154)

^{1}H- and ^{13}C-NMR data are given in Table 38.

Click reaction of 7-*O*-Propargylluaplbigenin (152) with 2-Azidoacetic acid (154)



(**152**) (**155**)

A freshly prepared solution of $CuSO_4 \cdot 5H_2O$ (12 mg, 0.05 mmol) and sodium ascorbate (5 mg, 0.02 mmol) in 1.0 ml of water was added to a solution of compound **152** (22.2 mg, 0.05 mmol) and 2-azidoacetic acid (**154**) (4.7 mg, 0.05 mmol) in THF/H_2O (9:1) (1.0 ml). The mixture was stirred at room temperature overnight. After completion of the reaction, cold water (3 ml) was added and the mixture was extracted with *n*-butanol (3x75 ml); the organic phase was washed with water, dried over anhydrous Na_2SO_4 and evaporated under reduce pressure to dryness. The crude mixture was separated

on reverse phase column eluting with H_2O-MeOH (60:40) to give the clicle product **155** (11.02 mg, 43%) as yellow solid.

7-*O*-[1′′′′-(Carboxymethyl)-1′′′′,*H*-3′′′′,4′′′′,5′′′′-triazole]lupalbigenin (155)

IR: ν_{max} 3382, 2971, 2924, 1614, 1510, 1486, 1450, 1390, 1270, 1219, 1172, 1113, 1061, 815 cm^{-1}.

^{1}H- and ^{13}C-NMR data are given in Table 39.

HR-TOFMS (ESI^-): *m/z* 544.2110 $[M-H]^-$ (Calcd. For $C_{30}H_{31}N_3O_7$–H, 544.2089).

Table 11 ^{1}H- and ^{13}C-NMR Data of Compound **1**

Position	Derrisisoflavone A (**1**)	
	^{1}H-NMR	^{13}C-NMR
2	7.82 (*s*)	150.7
3	-	126.7
4	-	176.1
5	-	156.1
6	-	119.4
7	-	158.0
8	-	111.5
9	-	155.0
10	-	112.8
1′	-	123.4
2′, 6′	7.30 (*d*, 7.3)	130.3
3′, 5′	6.83 (*d*, 7.3)	115.5
4′	-	156.5
1″	3.46 (*br d*, 7.2)	22.4
2″	5.18 (*br t*, 7.2)	121.6
3″	-	135.3
4″	1.79 (*s*)	18.0
5″	1.70 (*s*)	25.8
1‴	3.49 (*br d,* 7.7)	22.2
2‴	5.17 (*br t,*7.7)	121.1
3‴	-	134.3
4‴	1.79 (*s*)	17.9
5‴	1.69 (*s*)	25.7
5-OCH_3	3.77 (*s*)	62.4

Recorded in $CDCl_3$.

Table 12 ^{1}H- and ^{13}C-NMR Data of Compound **7**

Position	5,7,4′-Trihydroxy-6,8-diphenylisoflavone (**7**)	
	^{1}H-NMR	^{13}C-NMR
2	7.87 (*s*)	152.7
3	-	123.2
4	-	181.4
5	-	159.6
6	-	110.2
7	-	157.5
8	-	105.4
9	-	153.4
10	-	105.8
1′	-	123.0
2′, 6′	7.32 (*d*, 8.4)	130.3
3′, 5′	6.81 (*d*, 8.4)	115.7
4′	-	156.0
1″	3.44 (*br d*, 7.0)	21.6
2″	5.24 (*br t*, 7.0)	121.3
3″	-	135.5
4″	1.82 (*s*)	17.9
5″	1.75 (*s*)	25.7
1‴	3.46 (*br d*, 6.7)	21.6
2‴	5.20 (*br t*, 6.7)	121.4
3‴	-	134.1
4‴	1.81 (*s*)	17.9
5‴	1.72 (*s*)	25.8
5-OH	13.08 (*s*)	-
4′-OH	6.36 (*s*)	-

Recorded in $CDCl_3$.

Table 13 ^{1}H- and ^{13}C-NMR Data of Compound **8**

Position	Lupalbigenin (**8**)	
	^{1}H-NMR	^{13}C-NMR
2	7.77 (*s*)	152.5
3	-	123.0
4	-	181.0
5	-	159.6
6	-	110.5
7	-	161.4
8	6.35 (*s*)	93.7
9	-	156.1
10	-	105.8
1′	-	123.7
2′	7.22 (*br d*, 2.2)	130.3
3′	-	127.3
4′	-	154.7
5′	6.83 (*br d*, 8.7)	115.7
6′	7.22 (*br dd*, 8.7, 2.2)	128.1
1″	3.41 (*d*, 7.0)	21.5
2″	5.25 (*br t*, 7.0)	121.3
3″	-	134.9
4″	1.80 (*s*)	17.9
5″	1.72 (*s*)	25.8
1‴	3.36 (*d,* 7.2)	29.6
2‴	5.32 (*br t*, 7.2)	121.7
3‴	-	134.9
4‴	1.75 (*s*)	17.9
5‴	1.74 (*s*)	25.8
5-OH	13.17 (*s*)	-

Recorded in $CDCl_3$ + 3 drops of CD_3OD.

Table 14 ^{1}H- and ^{13}C-NMR Data of Compound **9**

Position	Scandinone (**9**)	
	^{1}H-NMR	^{13}C-NMR
2	7.80 (*s*)	150.3
3	-	125.7
4	-	175.7
5	-	158.0
6	-	121.7
7	-	155.9
8	-	105.8
9	-	152.1
10	-	112.6
1′	-	123.2
2′, 6′	7.29 (*d*, 8.4)	130.4
3′, 5′	6.82 (*d*, 8.4)	115.4
4′	-	156.7
1″	3.36 (*d*, 6.9)	22.1
2″	5.14 (*br t,* 6.9)	122.5
3″	-	131.4
4″	1.78 (*s*)	17.9
5″	1.65 (*s*)	25.6
1‴	6.74 (*d,* 10.0)	115.1
2‴	5.63 (*d*, 10.0)	128.8
3‴	-	77.8
4‴, 5‴	1.46 (*s*)	28.0
5-OCH_3	3.83 (*s*)	62.3
4′-OH	6.44 (*s*)	-

Recorded in $CDCl_3$ + 2 drops of CD_3OD.

Table 15 ^{1}H- and ^{13}C-NMR Data of Compound **28**

Position	Scanderone (**28**)	
	^{1}H-NMR	^{13}C-NMR
2	7.83 (*s*)	152.5
3	-	123.8
4	-	181.0
5	-	159.4
6	6.36 (*s*)	94.8
7	-	156.8
8	-	105.5
9	-	157.3
10	-	106.1
1′	-	122.4
2′	7.24 (*br s*)	130.3
3′	-	127.6
4′	-	154.7
5′	6.84 (*d*, 8.8)	115.5
6′	7.24 (*br d*, 8.8)	127.9
1″	6.75 (*d*, 10.0)	115.4
2″	5.65 (*d*,10.0)	128.1
3″	-	78.0
4″, 5″	1.50 (*s*)	28.2
1‴	3.39 (*d*, 7.1)	29.2
2‴	5.38 (*br t*, 7.1)	121.8
3‴	-	134.1
4‴	1.78 (*s*)	17.8
5‴	1.78 (*s*)	25.7
5-OH	13.21 (*s*)	-

Recorded in $CDCl_3$ + 2 drops of CD_3OD.

Table 16 ^{1}H- and ^{13}C-NMR Data of Compound **43**

Position	4′-*O*-Methylosajin (**43**)	
	^{1}H-NMR	^{13}C-NMR
2	7.88 (*s*)	152.5
3	-	123.1
4	-	181.2
5	-	154.7
6	-	107.4
7	-	156.8
8	-	105.4
9	-	154.9
10	-	105.9
1′	-	123.2
2′, 6′	7.44 (*d*, 8.0)	130.1
3′, 5′	6.96 (*d*, 8.0)	114.0
4′	-	159.7
1″	3.38 (*d*, 7.2)	21.3
2″	5.16 (*t*, 7.2)	122.0
3″	-	131.7
4″	1.79 (*s*)	17.9
5″	1.66 (*s*)	25.8
1‴	6.72 (*d*, 10.0)	115.8
2‴	5.60 (*d*, 10.0)	128.0
3‴	-	77.8
4‴, 5‴	1.45(*s*)	28.2
5-OH	13.09 (*s*)	-
4′-OCH_3	3.82 (*s*)	55.3

Recorded in $CDCl_3$.

Table 17 ^{1}H- and ^{13}C-NMR Data of Compound **44**

Position	Osajin (**44**)	
	^{1}H-NMR	^{13}C-NMR
2	7.87 (*s*)	152.8
3	-	122.7
4	-	181.5
5	-	157.0
6	-	107.5
7	-	154.8
8	-	105.5
9	-	152.8
10	-	105.9
1′	-	123.4
2′, 6′	7.29 (*d,* 8.4)	130.3
3′, 5′	6.78 (*d,* 8.4)	115.7
4′	-	156.2
1″	3.38 (*d,* 7.1)	21.3
2″	5.17 (*t,* 7.1)	121.9
3″	-	131.7
4″	1.80 (*s*)	17.9
5″	1.67 (*s*)	25.7
1‴	6.72 (*d*, 10.0)	115.8
2‴	5.61 (*d*, 10.0)	128.1
3‴	-	77.8
4‴, 5‴	1.45 (*s*)	28.2
5-OH	13.00 (*s*)	-

Recorded in $CDCl_3$.

Table 18 ^{1}H- and ^{13}C-NMR Data of Compound **51**

Position	Scandenin (**51**)	
	^{1}H-NMR	^{13}C-NMR
2	-	163.0
3	-	103.6
4	-	160.9
5	-	153.9
6	-	119.1
7	-	155.1
8	-	106.7
9	-	147.1
10	-	101.1
1′	-	123.1
2′, 6′	7.37 (*d,* 8.4)	131.8
3′, 5′	6.84 (*d,* 8.4)	115.2
4′	-	155.3
1″	3.31 (*d,* 6.3)	22.4
2″	5.14 (*br t,* 6.3)	122.0
3″	-	132.4
4″	1.84 (*s*)	18.0
5″	1.69 (*s*)	25.7
1‴	6.87 (*d,* 10.0)	115.3
2‴	5.67 (*d,* 10.0)	129.6
3‴	-	78.1
4‴, 5‴	1.45 (*s*)	28.0
5-OCH_3	3.90 (*s*)	63.9
4′-OH	10.18 (*s*)	-

Recorded in $CDCl_3$.

Table 19 ^{1}H- and ^{13}C-NMR Data of Compounds **124** and **125**

Position	Derrisisoflavone A 7-*O*-acetate (**124**)		Derrisisoflavone A 4′-*O*-acetate (**125**)	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
2	7.87 (*s*)	151.0	7.87 (*s*)	150.9
3	-	125.9	-	124.8
4	-	175.9	-	175.2
5	-	156.7	-	156.2
6	-	126.1	-	119.4
7	-	151.7	-	158.1
8	-	119.7	-	111.5
9	-	154.6	-	154.9
10	-	117.5	-	112.9
1′	-	123.6	-	129.8
2′, 6′	7.28 (*d*, 8.4)	130.4	7.55 (*dd*, 8.6, 2.0)	130.3
3′, 5′	6.77 (*d*, 8.4)	115.6	7.12 (*dd*, 8.6, 2.0)	121.5
4′	-	156.1	-	150.4
1″	3.32 (*br s*)	23.7	3.50 (*d*, 8.0)	22.7
2″	5.07 (*br t*, 7.0)	122.1	5.18 (*br t*, 8.0)	121.5
3″	-	132.2	-	135.6
4″	1.75 (*s*)	17.9	1.83 (*s*)	18.0
5″	1.66 (*s*)	25.6	1.74 (*s*)	25.8
1‴	3.36 (*br s*)	23.6	3.52 (*d*, 8.0)	22.2
2‴	5.10 (*br t*, 7.1)	120.6	5.23 (*br t*, 8.0)	121.0
3‴	-	132.9	-	134.5
4‴	1.76 (*s*)	17.9	1.82 (*s*)	18.0
5‴	1.68 (*s*)	25.6	1.72 (*s*)	25.8
5-OCH_3	3.82 (*s*)	62.6	3.80 (*s*)	62.4
4′-$\underline{CO}CH_3$	-	-	-	169.6
4′-$CO\underline{CH_3}$	-	-	2.29 (*s*)	21.2
7-$\underline{CO}CH_3$	-	168.7	-	-
7-$CO\underline{CH_3}$	2.33 (*s*)	20.6	-	-

Recorded in $CDCl_3$.

Table 20 ^{1}H- and ^{13}C-NMR Data of Compound **126**

Position	Derrisisoflavone A 7,4′-di-*O*-acetate (**126**)	
	^{1}H-NMR	^{13}C-NMR
2	7.91 (*s*)	151.3
3	-	125.3
4	-	175.2
5	-	156.7
6	-	126.2
7	-	151.8
8	-	119.7
9	-	154.5
10	-	117.5
1′	-	129.4
2′, 6′	7.54 (*d*, 8.4)	130.2
3′, 5′	7.13 (*d*, 8.4)	121.6
4′	-	150.6
1″	3.32 (*br s*)	23.6
2″	5.07 (*br t*, 6.5)	122.0
3″	-	132.1
4″	1.75 (*s*)	17.9
5″	1.66 (*s*)	25.6
1‴	3.37 (*br s*)	23.7
2‴	5.11 (*br t*, 6.9)	120.6
3‴	-	132.8
4‴	1.77 (*s*)	17.8
5‴	1.68 (*s*)	25.6
5-OCH_3	3.83 (*s*)	62.5
4′-$\underline{CO}CH_3$	-	169.4
4′-$CO\underline{CH_3}$	2.91 (*s*)	21.1
7-$\underline{CO}CH_3$	-	168.5
7-$CO\underline{CH_3}$	2.32 (*s*)	20.5

Recorded in $CDCl_3$.

Table 21 ^{1}H- and ^{13}C-NMR Data of Compounds **127** and **128**

Position	Lupalbigenin 7-*O*-acetate (**127**)		Lupalbigenin 4′-*O*-acetate (**128**)	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
2	7.87 (*s*)	153.3	7.82 (*s*)	153.1
3	-	124.0	-	123.3
4	-	181.5	-	180.6
5	-	160.1	-	159.7
6	-	117.3	-	110.2
7	-	154.1	-	161.5
8	6.69 (*s*)	101.1	6.35 (*s*)	94.0
9	-	154.7	-	156.1
10	-	109.3	-	105.9
1′	-	122.7	-	128.8
2′	7.22 (*br d*, 2.8)	130.5	7.34 (*br s*)	130.7
3′	-	127.2	-	133.4
4′	-	154.1	-	149.0
5′	6.82 (*d*, 8.4)	115.9	7.06 (*d*, 8.0)	122.5
6′	7.23 (*br dd*, 8.4, 2.8)	128.1	7.35 (*br d*, 8.0)	127.7
1″	3.30 (*d*, 6.7)	22.3	3.44 (*d*, 7.0)	21.5
2″	5.12 (*br t*, 6.7)	121.1	5.25 (*br t*, 7.0)	121.0
3″	-	132.5	-	136.1
4″	1.75 (*s*)	17.8	1.82 (*s*)	17.9
5″	1.66 (*s*)	25.7	1.75 (*s*)	25.8
1‴	3.37 (*d*, 7.0)	29.7	3.26 (*d*, 7.0)	28.9
2‴	5.32 (*br t*, 7.0)	121.5	5.21 (*br t*, 7.0)	121.3
3‴	-	135.0	-	133.8
4‴	1.77 (*s*)	17.9	1.68 (*s*)	17.9
5‴	1.75 (*s*)	25.8	1.71 (*s*)	25.7
5-OH	13.13 (*s*)	-	13.16 (*s*)	-
4′-$\underline{CO}CH_3$	-	-	-	169.5
4′-CO$\underline{CH_3}$	-	-	2.31 (*s*)	20.9
7-$\underline{CO}CH_3$	-	168.6	-	-
7-CO$\underline{CH_3}$	2.33 (s)	20.9	-	-

Recorded in $CDCl_3$.

Table 22 ^{1}H- and ^{13}C-NMR Data of Compound **129**

Position	Lupalbigenin 7,4′-*O*-diacetate (**129**)	
	^{1}H-NMR	^{13}C-NMR
2	7.91 (*s*)	153.7
3	-	123.6
4	-	181.1
5	-	160.1
6	-	117.5
7	-	154.6
8	6.71 (*s*)	101.2
9	-	154.2
10	-	109.2
1′	-	128.4
2′	7.34 (*br d*, 2.1)	130.6
3′	-	133.9
4′	-	149.1
5′	7.08 (*d*, 8.0)	122.5
6′	7.35 (*br dd*, 8.0, 2.1)	127.3
1″	3.31 (*d*, 6.9)	22.3
2″	5.12 (*dd*, 6.9, 1.2)	120.7
3″	-	132.5
4″	1.75 (*s*)	17.8
5″	1.67 (*s*)	25.6
1‴	3.37 (*d*, 7.1)	28.9
2‴	5.22 (*dd*, 7.1, 1.3)	121.0
3‴	-	133.5
4‴	1.72 (*s*)	17.8
5‴	1.69 (*s*)	25.6
5-OH	13.08 (*s*)	-
4′-$\underline{CO}CH_3$	-	169.3
4′-CO$\underline{CH_3}$	2.31 (*s*)	20.8
7-$\underline{CO}CH_3$	-	168.4
7-CO$\underline{CH_3}$	2.33 (s)	20.9

Recorded in $CDCl_3$.

Table 23 ^{1}H- and ^{13}C-NMR Data of Compound **130**

Position	Osajin 4′-*O*-acetate (**130**)	
	^{1}H-NMR	^{13}C-NMR
2	7.91 (*s*)	153.0
3	-	122.7
4	-	180.8
5	-	154.6
6	-	107.5
7	-	157.0
8	-	105.5
9	-	154.9
10	-	105.8
1′	-	128.6
2′, 6′	7.53 (*d*, 7.8)	130.0
3′, 5′	7.15 (*d*, 7.8)	121.8
4′	-	150.7
1″	3.38 (*d*, 7.1)	21.3
2″	5.16 (*t*, 7.1)	121.9
3″	-	131.7
4″	1.79 (*s*)	17.9
5″	1.67 (*s*)	25.8
1‴	6.72 (*d*, 10.0)	115.8
2‴	5.61 (*d*, 10.0)	128.1
3‴	-	77.8
4‴, 5‴	1.45(*s*)	28.2
5-OH	12.99 (*s*)	-
4′-$\underline{CO}CH_3$	-	169.4
4′-CO$\underline{CH_3}$	2.30 (*s*)	21.1

Recorded in $CDCl_3$.

Table 24 ^{1}H- and ^{13}C-NMR Data of Compounds **131** and **132**

Position	Derrisisoflavone A 7-*O*-methyl ether (**131**)		Derrisisoflavone A 4′-*O*-methyl ether (**132**)	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
2	7.89 (*s*)	151.1	7.84 (*s*)	150.4
3	-	125.8	-	125.2
4	-	176.4	-	175.6
5	-	161.2	-	156.2
6	-	127.1	-	119.2
7	-	156.9	-	157.9
8	-	119.9	-	111.5
9	-	155.3	-	154.9
10	-	116.0	-	113.0
1′	-	123.4	-	124.5
2′, 6′	7.28 (*d*, 8.5)	130.4	7.45 (*d*, 7.7)	130.3
3′, 5′	6.81 (*d*, 8.5)	115.7	6.94 (*d*, 7.7)	113.9
4′	-	156.3	-	159.4
1″	3.43 (*d*, 6.5)	23.3	3.50 (*d*, 7.4)	22.7
2″	5.19 (*br t*, 6.5)	123.3	5.19 (*br t*, 7.4)	121.6
3″	-	131.7	-	135.5
4″	1.79 (*s*)	17.9	1.82 (*s*)	18.0
5″	1.66 (*s*)	25.7	1.74 (*s*)	25.8
1‴	3.51 (*d*, 6.5)	23.1	3.50 (*d*, 7.4)	22.2
2‴	5.19 (*br t*, 6.5)	122.0	5.22 (*br t*, 7.4)	121.1
3‴	-	132.5	-	134.3
4‴	1.81 (*s*)	17.9	1.82 (*s*)	17.9
5‴	1.69 (*s*)	25.7	1.72 (*s*)	25.8
5-OCH_3	3.79 (*s*)	62.3	3.80 (*s*)	62.4
4′-OCH_3	-	-	3.80 (*s*)	55.3
7-OCH_3	3.84 (*s*)	62.0	-	-

Recorded in $CDCl_3$.

Table 25 ^{1}H- and ^{13}C-NMR Data of Compound **133**

Position	Derrisisoflavone A 7,4′-di-*O*-methyl ether (**133**)	
	^{1}H-NMR	^{13}C-NMR
2	7.88 (*s*)	150.8
3	-	127.1
4	-	175.7
5	-	157.1
6	-	126.3
7	-	161.0
8	-	119.8
9	-	155.3
10	-	115.2
1′	-	125.5
2′, 6′	7.45 (*d*, 7.8)	130.3
3′, 5′	6.94 (*d*, 7.8)	113.9
4′	-	159.5
1″	3.42 (*d*, 5.7)	23.3
2″	5.19 (*br t*, 5.7)	123.3
3″	-	131.7
4″	1.77 (*s*)	18.0
5″	1.66 (*s*)	25.7
1‴	3.51 (*d*, 6.2)	23.2
2‴	5.19 (*br t*, 6.2)	122.0
3‴	-	132.5
4‴	1.80 (*s*)	18.0
5‴	1.69 (*s*)	25.7
5-OCH_3	3.81 (*s*)	62.3
4′-OCH_3	3.81 (*s*)	55.3
7-OCH_3	3.78 (*s*)	62.0

Recorded in $CDCl_3$.

Table 26 ^{1}H- and ^{13}C-NMR Data of Compounds **134** and **135**

Position	Lupalbigenin 7-*O*-methyl ether (**134**)		Lupalbigenin 7,4′-*O*-dimethyl ether (**135**)	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
2	7.82 (*s*)	152.4	7.81 (*s*)	152.3
3	-	123.0	-	122.9
4	-	180.9	-	180.9
5	-	158.8	-	158.9
6	-	113.0	-	113.0
7	-	163.2	-	163.2
8	6.38 (*s*)	89.4	6.37 (*s*)	89.4
9	-	156.4	-	156.4
10	-	106.2	-	106.3
1′	-	123.9	-	124.0
2′	7.21 (*s*)	121.9	7.22 (*d*, 2.1)	129.7
3′	-	127.3	-	130.4
4′	-	154.7	-	157.5
5′	6.82 (*d*, 8.9)	115.9	6.89 (*d*, 8.4)	110.3
6′	7.23 (*br d*, 8.9)	128.1	7.33 (*dd*, 8.4, 2.1)	127.7
1″	3.35 (*br d*, 7.0)	21.4	3.35 (*br d*, 5.8)	21.4
2″	5.12 (*br t*, 7.0)	121.9	5.20 (*br t*, 5.8)	122.0
3″	-	132.0	-	131.9
4″	1.77 (*s*)	17.8	1.78 (*s*)	17.8
5″	1.66 (*s*)	25.8	1.66 (*s*)	25.8
1‴	3.34 (*br d*, 7.1)	29.7	3.33 (*br d*, 5.9)	28.5
2‴	5.32 (*br t*, 7.1)	121.6	5.30 (*br t*, 5.9)	122.3
3‴	-	134.8	-	132.7
4‴	1.77 (*s*)	17.9	1.72 (*s*)	17.8
5‴	1.76 (*s*)	28.8	1.70 (*s*)	25.8
5-OH	12.90 (*s*)	-	12.91 (*s*)	-
4′-OCH_3	-	-	3.84 (*s*)	55.5
7-OCH_3	3.87 (*s*)	55.9	3.88 (*s*)	55.9

Recorded in $CDCl_3$.

Table 27 ^{1}H- and ^{13}C-NMR Data of Compounds **136** and **137**

Position	Tetrahydroderrisisoflavone A (**136**)		Hexahydroderrisisoflavone A (**137**)	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
2α 2β	7.84 (*s*)	150.8	4.49 (*dd*, 11.2, 9.0) 4.51 (*dd*, 11.2, 5.2)	70.9
3	-	125.4	3.68 (*br dd*, 9.0, 5.2)	52.0
4	-	176.3	-	191.1
5	-	156.0	-	157.9
6	-	121.2	-	117.1
7	-	156.5	-	158.8
8	-	112.8	-	112.4
9	-	154.9	-	159.7
10	-	112.5	-	108.8
1′	-	123.4	-	127.0
2′, 6′	7.29 (*d*, 8.4)	130.4	7.03 (*d*, 8.3)	129.5
3′, 5′	6.81 (*d*, 8.4)	115.5	6.71 (*d*, 8.3)	115.6
4′	-	156.5	-	155.9
1″	2.67 (*dd*, 8.2, 3.0)	21.4	2.68 (*t*, 9.4)	21.0
2″	1.36-1.44 (*m*)[a]	38.9	1.29-1.31 (*m*)[a]	39.0
3″	1.58-1.65 (*m*)[b]	28.5	1.49-160 (*m*)	28.4
4″	0.95 (*s*)	22.4	0.90 (*s*)	22.4
5″	0.94 (*s*)	22.4	0.89 (*s*)	22.4
1‴	2.75 (*dd*, 8.0, 2.7)	21.0	2.54 (*t*, 8.7)	20.8
2‴	1.36-1.44 (*m*)[c]	38.1	1.30-1.32 (*m*)[b]	38.1
3‴	1.58-1.65 (*m*)[d]	28.3	1.49-1.60 (*m*)	28.1
4‴	0.97 (*s*)	22.3	0.90 (*s*)	22.4
5‴	0.95 (*s*)	22.3	0.89 (*s*)	22.4
5-OCH_3	3.83 (*s*)	62.4	3.71 (*s*)	61.7

Recorded in $CDCl_3$ + 2 drops of CD_3OD.

[a,b,c,d]Partially overlapping signals.

Table 28 ^{1}H- and ^{13}C-NMR Data of Compounds **138** and **139**

Position	Dihydrolupalbigenin (**138**)		Tetrahydrolupalbigenin (**139**)	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
2	7.80 (*s*)	152.6	7.75 (*s*)	154.2
3	-	123.1	-	123.5
4	-	181.0	-	182.6
5	-	159.6	-	160.7
6	-	109.9	-	114.7
7	-	161.4	-	163.8
8	6.36 (*s*)	94.0	6.28 (*s*)	94.3
9	-	156.1	-	157.7
10	-	105.9	-	106.5
1′	-	123.6	-	125.2
2′	7.23 (*br s*)	130.6	7.18 (*d*, 1.8)	131.9
3′	-	129.1	-	131.1
4′	-	153.7	-	156.6
5′	6.64 (*d*, 8.1)	115.4	6.73 (*d*, 8.2)	116.3
6′	7.20 (*br d*, 8.1)r	127.7	7.14 (*dd*, 8.2, 1.8)	128.8
1″	3.45 (*d*, 7.1)	21.5	2.63 (*dd*, 7.9, 2.4)	21.6
2″	5.26 (*br t*, 7.1)	121.0	1.36-1.40 (*m*)	39.2
3″	-	136.2	1.52-1.63 (*m*)	29.4
4″	1.82 (*s*)	17.9	0.94 (*s*)	23.6
5″	1.76 (*s*)	25.8	0.91 (*s*)	23.6
1‴	2.61 (*t*, 8.2)	27.8	2.59 (*dd*, 8.2, 2.4)	29.3
2‴	1.47-1.53 (*m*)	38.8	1.44-1.50 (*m*)	40.4
3‴	1.55-1.65 (*m*)	28.0	1.52-1.63 (*m*)	29.6
4‴	0.94 (*s*)	22.5	0.92 (*s*)	23.6
5‴	0.93 (*s*)	22.5	0.92 (*s*)	23.6
5-OH	13.23 (*s*)	-	13.05(*s*)	-

Compound **138** recorded in $CDCl_3$.

Compound **139** recorded in CD_3OD + $CDCl_3$.

Table 29 ^{1}H- and ^{13}C-NMR Data of Compound **140**

Position	Hexahydrolupalbigenin (**140**)	
	^{1}H-NMR	^{13}C-NMR
2α	4.47 (*dd*, 11.0, 9.3)	71.4
2β	4.52 (*dd*, 11.0, 5.3)	
3	3.85 (*dd*, 9.3, 5.3)	50.7
4	-	197.0
5	-	162.1
6	-	109.5
7	-	162.3
8	5.90 (*s*)	94.5
9	-	160.6
10	-	103.0
1′	-	129.5
2′	6.99 (*br s*)	130.3
3′	-	126.9
4′	-	153.2
5′	6.69 (*d*, 8.1)	115.6
6′	6.94 (*d*, 8.1)	126.9
1″	2.51 (*t*, 8.2)	19.8
2″	1.35-1.39 (*m*)	37.9
3″	1.56-1.63 (*m*)	28.2
4″	0.94 (*s*)	22.5
5″	0.91 (*s*)	28.0
1‴	2.55 (*t*, 8.1)	27.8
2‴	1.44-1.48 (*m*)	38.7
3‴	1.56-1.63 (*m*)	28.2
4‴	0.92 (*s*)	22.5
5‴	0.92 (*s*)	28.0
5-OH	12.36 (*s*)	-

Recorded in $CDCl_3$.

Table 30 ^{1}H- and ^{13}C-NMR Data of Compounds **141** and **142**

Position	Tetrahydroosajin (**141**)		Hexahydroosajin (**142**)	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
2α	7.87 (*s*)	152.8	4.43 (*dd*, 11.3, 8.5)	71.2
2β			4.52 (*dd*, 11.3, 5.0)	
3	-	123.1	3.84 (*dd*, 8.5, 5.0)	50.6
4	-	181.5	-	197.4
5	-	157.2	-	159.6
6	-	108.4	-	109.4
7	-	158.1	-	161.0
8	-	104.6	-	101.6
9	-	153.1	-	157.2
10	-	104.9	-	101.9
1′	-	122.8	-	127.2
2′, 6′	7.32 (*d*, 8.5)	130.3	7.07 (*d*, 8.4)	129.8
3′, 5′	6.90 (*d*, 8.5)	115.7	6.71 (*d*, 8.4)	115.8
4′	-	156.1	-	155.4
1″	2.68 (*br t*, 7.9)	20.0	2.49 (*br t*, 7.8)	19.9
2″	1.30-1.39 (*m*)[a]	38.6	1.33-1.26 (*m*)	38.6
3″	1.51-1.60 (*m*)	27.9	1.47-1.52 (*m*)	27.8
4″	0.95 (*s*)	22.6	0.92 (*s*)	22.6
5″	0.93 (*s*)	22.6	0.90 (*s*)	22.7
1‴	2.72 (*t*, 6.8)	16.3	2.60 (*t*, 6.8)	15.9
2‴	1.80 (*t*, 6.8)	31.6	1.76 (*t*, 6.8)	31.6
3‴	-	75.8	-	76.1
4‴, 5‴	1.35 (*s*)	26.8	1.33 (*s*)	26.8
5-OH	13.06 (*s*)	-	12.43 (*s*)	-

Recorded in $CDCl_3$.

[a]Partially overlapping signals.

Table 31 ^{1}H- and ^{13}C-NMR Data of Compound **143**

Position	Tetrahydrolupalbigenin 7-*O*-methyl ether (**143**)	
	^{1}H-NMR	^{13}C-NMR
2	7.82 (*s*)	152.3
3	-	123.3
4	-	180.9
5	-	158.9
6	-	114.4
7	-	163.4
8	6.38 (*s*)	89.2
9	-	156.2
10	-	106.1
1′	-	123.9
2′	7.23 (*br s*)	130.6
3′	-	129.1
4′	-	153.7
5′	6.77 (*d*, 8.1)	115.4
6′	7.20 (*br d*, 8.1)	127.7
1″	2.63 (*m*)[a]	20.2
2″	1.34-1.39 (*m*)	37.8
3″	1.65-1.54 (*m*)	28.0
4″	0.95 (*s*)	22.5
5″	0.94 (*s*)	22.5
1‴	2.62 (*m*)[b]	27.8
2‴	1.47-1.54 (*m*)	38.8
3‴	1.65-1.45 (*m*)	28.2
4‴	0.94 (*s*)	22.6
5‴	0.93 (*s*)	22.6
5-OH	12.88 (*s*)	-
7-OCH_3	3.83 (*s*)	55.8

Recorded in $CDCl_3$.

[a,b]Partially overlapping signals.

Table 32 ^{1}H- and ^{13}C-NMR Data of Compounds **144** and **145**

Position	Derrisisoflavone A 7-*O*-propanoate (**144**)		Derrisisoflavone A- 4′-*O*-propanoate (**145**)	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
2	7.86 (*s*)	151.0	7.86 (*s*)	150.9
3	-	126.1	-	129.7
4	-	176.0	-	175.2
5	-	156.1	-	156.3
6	-	119.8	-	119.5
7	-	151.8	-	158.0
8	-	115.5	-	111.5
9	-	154.6	-	154.9
10	-	117.4	-	113.0
1′	-	123.5	-	124.9
2′, 6′	7.28 (*d*, 8.0)	130.4	7.54 (*d*, 8.4)	130.2
3′, 5′	6.77 (*d*, 8.0)	115.5	7.12 (*d*, 8.4)	121.5
4′	-	156.6	-	150.6
1″	3.34 (*br s*)	23.6	3.51 (*d*, 7.4)	22.7
2″	5.05 (*br t*, 9.6)	122.1	5.19 (*br t*, 7.4)	121.6
3″	-	132.2	-	135.4
4″	1.73 (*s*)	17.9	1.83 (*s*)	17.9
5″	1.65 (*s*)	25.6	1.74 (*s*)	25.8
1‴	3.34 (*br s*)	23.5	3.51 (*d*, 7.4)	22.2
2‴	5.09 (*br t*, 8.5)	119.8	5.23 (*br t*, 7.4)	121.1
3‴	-	132.9	-	134.4
4‴	1.75 (*s*)	17.9	1.83 (*s*)	17.9
5‴	1.67 (*s*)	25.6	1.72 (*s*)	25.8
5-OCH_3	3.81 (*s*)	62.5	3.81 (*s*)	62.4
4′-$\underline{CO}CH_2CH_3$	-	-	-	172.9
4′-$CO\underline{CH_2}CH_3$	-	-	2.58 (*q*, 7.5)	27.8
4′-$COCH_2\underline{CH_3}$	-	-	1.25 (*t*, 7.5)	9.0
7-$\underline{CO}CH_2CH_3$	-	172.3	-	-
7-$CO\underline{CH_2}CH_3$	2.63 (*q*, 7.6)	27.4	-	-
7-$COCH_2\underline{CH_3}$	1.27 (*t*, 7.6)	9.0	-	-

Recorded in $CDCl_3$.

Table 33 ^{1}H- and ^{13}C-NMR Data of Compound **146**

Position	Derrisisoflavone A 7,4′-di-*O*-propanonate (**146**)	
	^{1}H-NMR	^{13}C-NMR
2	7.91 (*s*)	151.3
3	-	125.4
4	-	175.3
5	-	156.7
6	-	126.3
7	-	151.9
8	-	119.8
9	-	154.5
10	-	117.5
1′	-	128.9
2′. 6′	7.54 (*d*, 8.5)	130.2
3′, 5′	7.13 (*d*, 8.5)	121.6
4′	-	150.7
1″	3.30 (*br s*)	23.7
2″	5.06 (*br t*, 6.6)	122.1
3″	-	132.8
4″	1.73 (*s*)	17.9
5″	1.65 (*s*)	25.6
1‴	3.36 (*br s*)	23.6
2‴	5.10 (*br t*, 6.7)	120.7
3‴	-	133.4
4‴	1.76 (*s*)	17.9
5‴	1.68 (*s*)	25.6
5-OCH_3	3.83 (*s*)	62.5
4′-$\underline{CO}CH_2CH_3$	-	172.0
4′-$CO\underline{CH_2}CH_3$	2.56 (*q*, 7.4)	27.4
4′-$COCH_2\underline{CH_3}$	1.25 (*t*, 7.4)	9.1
7-$\underline{CO}CH_2CH_3$	-	172.9
7-$CO\underline{CH_2}CH_3$	2.62 (*q*, 7.4)	27.8
7-$COCH_2\underline{CH_3}$	1.27 (*t*, 7.4)	9.0

Recorded in $CDCl_3$.

Table 34 ^{1}H- and ^{13}C-NMR Data of Compound **147**

Position	5′-Nitrolupalbigenin (**147**)	
	^{1}H-NMR	^{13}C-NMR
2	7.81 (*s*)	152.8
3	-	122.8
4	-	180.1
5	-	159.5
6	-	111.7
7	-	161.8
8	6.32 (*s*)	93.6
9	-	155.9
10	-	105.3
1′	-	121.7
2′	7.58 (*d*, 1.9)	137.7
3′	-	133.7
4′	-	153.3
5′	-	133.1
6′	8.07 (*d*, 1.9)	122.6
1″	3.36 (*d*, 6.9)	21.4
2″	5.22 (*br t*, 6.9)	121.4
3″	-	133.6
4″	1.78 (*s*)	17.8
5″	1.72 (*s*)	25.7
1‴	3.41 (*dd*, 7.3, 1.2)	28.1
2‴	5.82 (*br t*, 7.3)	120.3
3‴	-	134.5
4‴	1.69 (*s*)	17.8
5‴	1.69 (*s*)	25.7
4′-OH	10.96	-
5-OH	12.82 (*s*)	-

Recorded in $CDCl_3$ + 2 drops of CD_3OD.

Table 35 ^{1}H- and ^{13}C-NMR Data of Compounds **148** and **149**

Position	2‴,3‴-Epoxylupalbigenin (**148**)		2″,3″,2‴,3‴-Diepoxylupalbigenin (**149**)	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
2	7.80 (*s*)	152.6	7.79 (*s*)	152.8
3	-	123.1	-	123.0
4	-	180.9	-	181.0
5	-	159.6	-	160.1
6	-	109.9	-	103.2
7	-	161.4	-	159.2
8	6.36 (*s*)	94.0	6.36 (*s*)	94.8
9	-	156.1	-	156.0
10	-	105.9	-	105.3
1′	-	123.5	-	123.3
2′	7.24 (*br s*)	130.8	7.22 (*br s*, 2.2)	130.7
3′	-	118.9	-	119.1
4′	-	153.1	-	153.1
5′	6.88 (*d*, 8.2)	117.5	6.86 (*d*, 8.3)	117.4
6′	7.23 (*br d*, 8.2 2.2)	128.4	7.20 (*dd*, 8.3, 2.2)	128.3
1″a	3.44 (*d*, 7.0)	21.5	2.71 (*dd*, 17.2, 5.9)	25.3
1″b			2.95 (*dd*, 17.2, 5.1)	
2″	5.26 (*br t*, 7.0)	121.0	3.84 (*dd*, 5.9, 5.1)	69.4
3″	-	136.2	-	78.5
4″	1.82 (*s*)	17.9	1.36 (*s*)	21.9
5″	1.75 (*s*)	25.8	1.34 (*s*)	24.8
1‴a	2.81 (*dd*, 16.9, 5.7)	31.4	2.80 (*dd*, 16.8, 5.6)	31.3
1‴b	3.11 (*dd*, 16.9, 4.5)		3.09 (*dd*, 16.8, 4.8)	
2‴	3.81 (*br dd*, 5.7, 4.5)	69.6	3.79 (*dd*, 5.6, 4.8)	68.5
3‴	-	76.7	-	77.2
4‴	1.37 (*s*)	22.3	1.35 (*s*)	22.2
5‴	1.34 (*s*)	24.6	1.31 (*s*)	24.8
5-OH	13.20 (*s*)	-	13.15 (*s*)	-

Compound **148** recorded in $CDCl_3$.

Compound **149** recorded in CD_3OD.

Table 36 ^{1}H- and ^{13}C-NMR Data of Compounds **150** and **151**

Position	Lupalbigenin 7-*O*-benzoate (**150**)		Lupalbigenin 7,4′-di-*O*-benzoate (**151**)	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
2	7.89 (*s*)	153.3	7.97 (*s*)	153.9
3	-	122.7	-	123.7
4	-	181.6	-	181.2
5	-	160.1	-	160.1
6	-	117.6	-	117.8
7	-	154.8	-	154.7
8	6.81 (*s*)	101.3	6.85 (*s*)	101.4
9	-	154.7	-	154.6
10	-	109.3	-	109.3
1′	-	124.0	-	128.5
2′	7.24 (*br s*)	130.5	7.42 (*br s*)	130.7
3′	-	127.2	-	133.5
4′	-	154.5	-	149.4
5′	6.84 (*d*, 8.6)	115.9	7.23 (*d*, 8.5)	122.7
6′	7.24 (*br s*)	128.2	7.43 (*br d*, 8.5)	127.6
1″	3.37 (*d*, 6.6)	22.4	3.38 (*d*, 6.8)	22.4
2″	5.14 (*br t*, 6.6)	121.1	5.15 (*br t*, 6.8)	121.1
3″	-	132.6	-	132.6
4″	1.57 (*s*)	17.8	1.57 (*s*)	17.8
5″	1.55 (*s*)	25.6	1.65 (*s*)	25.6
1‴	3.38 (*d*, 6.8)	29.8	3.34 (*d*, 7.1)	29.1
2‴	5.33 (*br t*, 6.8)	121.5	5.25 (*br t*, 7.1)	121.3
3‴	-	135.1	-	134.2
4‴	1.77 (*s*)	17.9	1.57 (*s*)	17.8
5‴	1.76 (*s*)	25.8	1.57 (*s*)	25.6
1⁗	-	164.4	-	164.3
2⁗	-	128.8	-	128.8
3⁗, 7⁗	8.19 (*d*, 7.7)	130.3	8.19-8.21 (*m*)[a]	130.3
4⁗, 6⁗	7.52 (*t*, 7.7)	128.2	7.54 (*t*, 7.8)	128.6
5⁗	7.66 (*t*, 7.7)	134.0	7.66 (*t*, 7.8)	134.0
8⁗	-	-	-	165.0
9⁗	-	-	-	129.3

Table 36 (continued)

Position	Lupalbigenin 7-*O*-benzoate (**150**)		Lupalbigenin 7,4′-di-*O*-benzoate (**151**)	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
10′′′, 14′′′′	-	-	8.19-8.21 (*m*)[b]	130.2
11′′′, 13′′′′	-	-	7.52 (*t*, 7.9)	128.7
12′′′′	-	-	7.64 (*t*, 7.9)	133.6
5-OH	13.17 (*s*)	-	13.14 (*s*)	-

Recorded in $CDCl_3$.

[a,b]Partially overlapping signals.

Table 37 ^{1}H- and ^{13}C-NMR Data of Compounds **152** and **153**

Position	7-*O*-Propargyllupalbigenin (**152**)		7,4′-Di-*O*-propargyllupalbigenin (**153**)	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
2	7.83 (*s*)	152.5	7.83 (*s*)	152.6
3	-	123.0	-	123.8
4	-	180.9	-	180.9
5	-	159.1	-	159.2
6	-	113.5	-	113.6
7	-	160.9	-	161.0
8	6.50 (*s*)	90.6	6.49 (*s*)	90.7
9	-	156.0	-	156.0
10	-	106.6	-	106.7
1′	-	123.9	-	123.9
2′	7.22 (*d*, 2.2)	130.6	7.24 (*d*, 2.2)	130.2
3′	-	127.1	-	131.1
4′	-	154.7	-	155.6
5′	6.83 (*d*, 8.8)	115.9	7.00 (*d*, 8.4)	111.9
6′	7.22 (*dd*, 8.8 2.2)	128.2	7.32 (*dd*, 8.4, 2.2)	127.6
1″	3.36 (*br d*, 7.2)	21.5	3.36 (*br d*, 7.2)	21.5
2″	5.20 (*dddd*, 8.7, 7.2, 2.6, 1.3)	121.7	5.21 (*dddd*, 8.7, 7.2, 2.7, 1.4)	121.7
3″	-	132.1	-	132.2
4″	1.78 (*s*)	17.9	1.79 (*s*)	17.9
5″	1.75 (*s*)	25.8	1.66 (*s*)	25.9
1‴	3.37 (*br d*, 7.2)	29.8	3.36 (*br d*, 7.3)	28.6
2‴	5.32 (*dddd*, 8.7, 7.2, 2.7, 1.3)	121.5	5.30 (*dddd*, 8.9, 7.3, 2.7, 1.4)	122.0
3‴	-	135.1	-	132.1
4‴	1.77 (*s*)	17.9	1.72 (*s*)	17.9
5‴	1.66 (*s*)	25.8	1.71 (*s*)	25.9
5-OH	12.94 (*s*)	-	12.97 (*s*)	-
7-O$\underline{CH_2}$C≡CH	4.77 (*d*, 2.4)	56.2	4.76 (*d*, 2.4)	56.3
7-OCH$_2\underline{C}$≡CH	-	77.6	-	77.7
7-OCH$_2$C≡$\underline{CH}$	2.55 (*t*, 2.4)	76.2	2.55 (*t*, 2.4)	76.3
4′-O$\underline{CH_2}$C≡CH	-	-	4.72 (*d*, 2.4)	56.1

Table 37 (continued)

Position	7-*O*-Propargyllupalbigenin (**152**)		7,4′-Di-*O*-propargyllupalbigenin (**153**)	
	^{1}H-NMR	^{13}C-NMR	^{1}H-NMR	^{13}C-NMR
4′-OCH$_2$C≡CH	-	-	-	78.8
4′-OCH$_2$C≡CH	-	-	2.50 (*t*, 2.4)	75.5

Recorded in $CDCl_3$.

Table 38 ^{1}H- and ^{13}C-NMR Data of Compound **154**

Position	2-Azidiacetic acid (**154**)	
	^{1}H-NMR	^{13}C-NMR
1	-	173.8
2	3.94 (*s*)	50.0
3-OH	9.33 (*s*)	-

Recorded in $CDCl_3$.

Table 39 ^{1}H- and ^{13}C-NMR Data of Compound **155**

Position	7-*O*-[1′′′′-(Carboxymethyl)-1′′′′,*H*-3′′′′,4′′′′,5′′′′-triazole]lupalbigenin (**155**)	
	^{1}H-NMR	^{13}C-NMR
2	8.13 (*s*)	155.1
3	-	123.4
4	-	182.7
5	-	159.9
6	-	114.4
7	-	163.6
8	6.85 (*s*)	92.1
9	-	158.0
10	-	107.5
1′	-	125.5
2′	7.26 (*d*, 2.2)	131.6
3′	-	129.6
4′	-	156.8
5′	6.86 (*br d*, 8.2)	115.9
6′	7.20 (*dd*, 8.2, 2.2)	128.9
1′′	3.31 (*m*)[a]	22.5
2′′	5.18 (*br t*, 7.3)	123.2
3′′	-	132.6
4′′	1.67 (*s*)	18.1
5′′	1.64 (*s*)	26.1
1′′′	3.33 (*m*)[b]	29.5
2′′′	5.37 (*dddd*, 8.3, 7.3, 3.6, 1.3)	124.6
3′′′	-	133.3
4′′′	1.76 (*s*)	18.1
5′′′	1.76 (*s*)	26.2
1′′′′	5.32 (*s*)	63.3
2′′′′	-	143.9
3′′′′	8.09 (*s*)	127.2
4′′′′	5.02 (*s*)	54.7
5′′′′	-	172.9
5-OH	-	-

Recorded in CD_3OD.

[a,b]Partially overlapping signals.

Anti-Cholinesterase Activities

Evaluation of anti-ChE activity by samples was measured by a microplate assay based on Ellman'man method[17] with modification. In brief, 140 µl of 10 mM sodium phosphate buffer (pH 8.0), 20 µl of solution of BuChE (0.2 units/mL in 10 mM sodium phosphate buffer, pH 8.0) and 20 µl of test compound solution dissolved in 80% methanol (a final concentration of 0.1 mg/mL) were mixed in 96-well plates and the plates were immediately shaken speed for 10 min.

The reaction was stated by adding 20 µl of mixture solution of 5 mM 5,5′-dithiobis-(2-nitrobenzoic acid) (DTNB) in 10 mM sodium phosphate buffer (pH 8.0), containing 0.1% bovine serum albumin (BSA) and 5 mM S-butyrylthiocholine iodide (BTCI) in 10 mM sodium phosphate buffer, pH 8.0 (5:1). The hydrolysis of butyryltriocholine was monitored at 405 nm after 5 minutes of incubation at room temperature. Percentage of inhibition was calculated by comparing the rate of enzymatic hydrolysis of BTCI for the sample that of blank (80% methanol in buffer). Galantamine was used as a reference standard. Every experiment was done in triplicate.

Table 40 Anti-cholinesterase Activities of Some Compounds Isolated from *D. scandens*

Compound	Butyrylcholinesterase
	IC_{50} (μM) ± S.D.
1	27.20 ± 0.55
7	1.44 ± 0.04
8	2.19 ± 0.10
9	177.20 ± 29.57
28	Inactive
44	19.14 ± 3.19
51	Inactive
Galantamine	3.10 ± 0.02

Data are the average of 3 independent experiments, given as IC_{50} values in μM ± S.D.; Inactive at 0.1 mg/ml; Galantamine is the reference drug.

Table 41 Anti-cholinesterase Activities of Modified Analogues

Compound	Butyrylcholinesterase
	IC_{50} (μM) ± S.D.
43	Inactive
124	6.07 ± 0.52
125	16.04 ± 0.89
126	Inactive
127	54.60 ± 5.75
128	55.56 ± 0.21
129	Inactive
130	Inactive
131	31.78 ± 8.40
132	27.44 ± 0.95
133	12.58 ± 0.13
134	62.98 ± 11.05
135	Inactive
136	2.53 ± 0.06
137	61.34 ± 3.22
138	0.64 ± 0.01
139	6.64 ± 0.39
140	4.73 ± 0.10
141	177.47 ± 31.26
142	Inactive
143	62.28 ± 8.24
144	10.31 ± 3.22
145	Inactive
146	Inactive
147	7.83 ± 0.73

Table 41 (continued)

Compound	Butyrylcholinesterase
	IC_{50} (μM) ± S.D.
148	28.15 ± 3.29
149	146.45 ± 14.86
150	7.48 ± 0.97
151	Inactive
152	Inactive
153	Inactive
155	Inactive
Galantamine	3.10 ± 0.02

Data are the average of 3 independent experiments, given as IC_{50} values in μM ± S.D.; Inactive at 0.1 mg/ml; Galantamine is the reference drug.

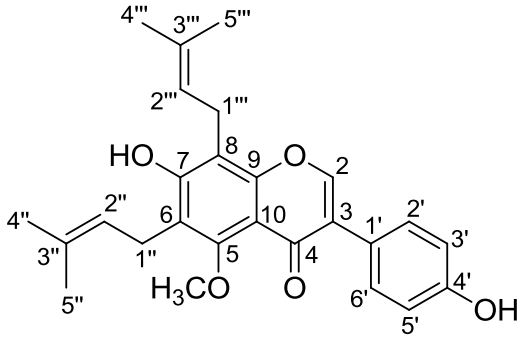
CHAPTER 3

RESULTS AND DISCUSSION

Chemical Constituents of *Derris scandens*

Investigation of the stems of *Derris scandens* Benth. resulted in the isolation of seven compounds. These included derrisisoflavone A (**1**), 5,7,4′-trihydroxy-6,8-diprenylisoflavone (**7**), lupalbienin (**8**), scandinone (**9**), scanderone (**28**), osajin (**44**) and scandenin (**51**).

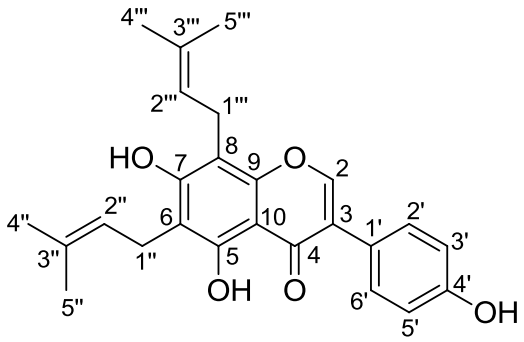
Derrisisoflavone A (1)



Compound **1** was obtained as yellow amorphous solid. The IR absorption bands indicated the presence of hydroxyl group (3162 cm^{-1}), conjugated carbonyl group (1630 cm^{-1}) and aromatic nucleus (1607 and 1583 cm^{-1}). The electrospray ionization mass spectrum (ESIMS) showed the $[M-H]^-$ peak at *m/z* 419, corresponding to the molecular formula of $C_{26}H_{28}O_5$. The ^1H- and ^{13}C-NMR data of **1** ($CDCl_3$, Table 11) showed a typical signal at δ 7.82 (1H, *s*, H-

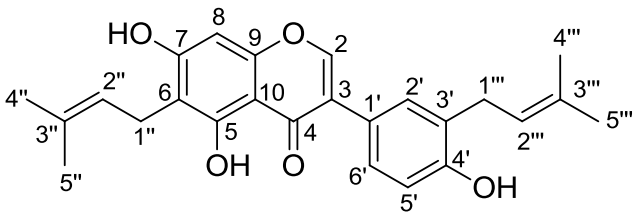
2) and ^{13}C-NMR signals (Table 11) at δ 150.7 (C-2), 126.7 (C-3) and 176.1 (C-4) were typical of an isoflavone. The presence of two symmetrical doublets (*J* = 7.3 Hz) at δ 7.30 and 6.83 corresponding to four protons on the *para*-substituted benzene of ring B. Furthermore, the ^{1}H-NMR spectrum showed two isoprenyl moieties attached to C-6 and C-8 at δ 1.79 (6H, *s*, H-4″, 4‴), 1.70 (3H, *s*, H-5″) and 1.69 (3H, *s*, H-5‴), two methine signals at δ 5.18 (1H, *br t*, *J* = *7.2* Hz, H-2″) and 5.17 (1H, *br t*, *J* = 7.7 Hz, H-2‴), two methylene signals at δ 3.49 (2H, *br d*, *J* = 7.7 Hz, H-1‴) and 3.46 (2H, *br d*, *J* = 7.2 Hz, H-1″). The methoxyl group at δ 3.77 were placed at position C-5 from HMBC correlations. The spectroscopic data led to the identification of **1** as derrisisoflavone A. The structure of this compound was confirmed by comparison of spectroscopic data with those of the literature values.[2]

5,7,4′-Trihydroxy-6,8-diprenylisoflavone (7)



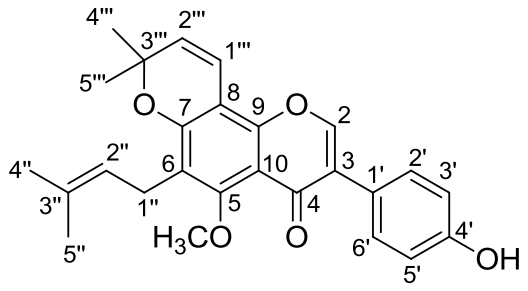
Compound **7** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3347 cm^{-1}), conjugated carbonyl group (1643 cm^{-1}) and aromatic nucleus (1611 and 1557 cm^{-1}). The ESIMS showed $[M-H]^-$ at *m/z* 405, corresponding to the molecular formula of $C_{25}H_{26}O_5$. The ^{1}H- and ^{13}C-NMR feature of **7** ($CDCl_3$, Table 12) were similar to those of derrisisoflavone A (**1**), the significant difference of which was the absence of the methoxyl signal and the presence of chelated hydroxyl signal at δ 13.08 (1H, *s*). The structure of this compound was confirmed by comparison of spectroscopic data with those of the literature values.[2] Compound **7** was therefore concluded to be 5,7,4′-trihydroxy-6,8-diprenylisoflavone.

Lupalbigenin (8)



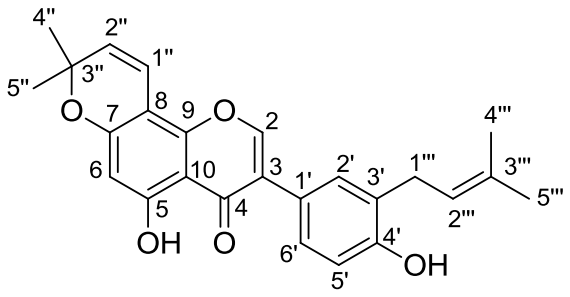
Compound **8** was obtained as pale yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3244 cm^{-1}), conjugated carbonyl group (1652 cm^{-1}) and aromatic nucleus (1618 and 1559 cm^{-1}). The ESIMS showed $[M-H]^-$ at *m/z* 405, corresponding to the molecular formula of $C_{25}H_{26}O_5$. The ^{1}H- and ^{13}C-NMR spectra of **8** ($CDCl_3$ +3 drops of CD_3OD, Table 13) showed similar patterns to those of 5,7,4′-trihydroxy-6,8-diprenylisoflavone (**7**). This difference could only be due to the attachment of the second isoprenyl moiety at C-3′, not at the C-8 position as that of 7. The postulation was supported by the HMBC correlations. The structure of this compound was confirmed by comparison of spectroscopic data with those of the literature values.[2] Compound **8** was therefore concluded to be lupalbigenin.

Scandinone (9)



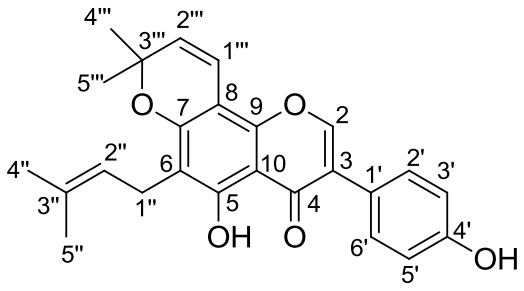
Compound **9** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3369 cm^{-1}), conjugated carbonyl group (1627 cm^{-1}) and aromatic nucleus (1606 and 1571 cm^{-1}). The ESIMS showed $[2M+Na]^+$ at *m/z* 859, corresponding to the molecular formula of $C_{26}H_{26}O_5$. The ^{1}H- and ^{13}C-NMR spectra of **9** ($CDCl_3$ + 2 drops of CD_3OD, Table 14) showed similar patterns to those of **1**, the significant difference of which was the absence of one isoprenyl signal and the presence of dimethylchromene ring which was determined from the resonance of two methyl groups at δ 1.46 (2×3H, *s*, H-4‴, H-5‴) and two *cis*-olefinic protons at δ 5.63 (1H, *d*, *J* = 10.0 Hz, H-2‴) and 6.74 (1H, *d*, *J* = 10.0 Hz, H-1‴). The location of dimethylchromene ring on C-8 (δ 105.8) and its ether linkage on C-7 (δ 155.9) of ring B was confirmed by HMBC, in which olefinic proton 1‴ was correlated to C-8 and C-7. The structure of this compound was confirmed by comparison of spectroscopic data with those of the literature values.[2] Compound **9** was therefore concluded to be scandinone.

Scanderone (28)



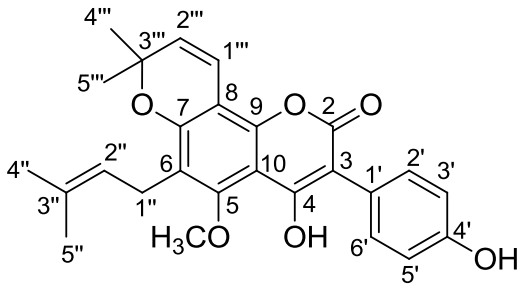
Compound **28** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3333 cm^{-1}), conjugated carbonyl group (1649 cm^{-1}) and aromatic nucleus (1617 and 1570 cm^{-1}). The ESIMS showed $[M-H]^-$ at *m/z* 403, corresponding to the molecular formula of $C_{25}H_{24}O_5$. The ^{1}H- and ^{13}C-NMR feature of **28** ($CDCl_3$ + 2 drops of CD_3OD, Table 15) were similar to those of scandinone (**9**), the significant difference of which was the prenyl unit placed at C-3′, whereas the correlations of H-1‴ to 2′ and 4′ were observed in the HMBC spectrum. In addition, in the ^{1}H-NMR spectrum the absence of the methoxyl signal and the presence of chelated OH signal (δ 13.21) were noted. The structure of this compound was confirmed by comparison of spectroscopic data with those of the literature values.[4] Compound **28** was therefore concluded to be scanderone.

Osajin (44)



Compound **44** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3414 cm^{-1}), conjugated carbonyl group (1642 cm^{-1}) and aromatic nucleus (1617, 1572 and 1513 cm^{-1}). The ESIMS showed $[M-H]^-$ at *m/z* 403, corresponding to the molecular formula of $C_{25}H_{24}O_5$. The ^{1}H- and ^{13}C-NMR feature of **44** ($CDCl_3$, Table 17) showed similar pattern of those of scandinone (**9**). The significant difference was the absence of the methoxyl group and the presence of chelated hydroxyl group at δ 13.00 (1H, *s*). From the spectroscopic data, compound **44** was therefore concluded to be osajin. This compound was identified by comparison of spectroscopic data with the literature values.[19]

Scandenin (51)

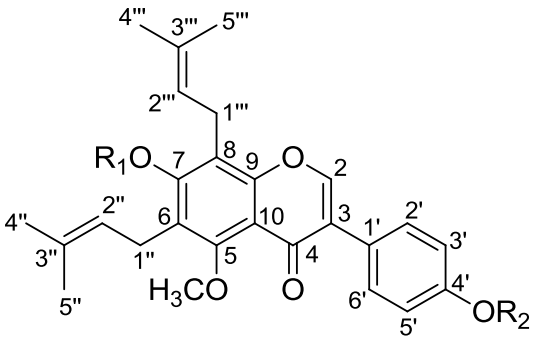


Compound **51** was obtained as white amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3216 cm^{-1}), unsaturated ketone (1679 cm^{-1}) and aromatic nucleus (1614, 1588 and 1517 cm^{-1}). The ESIMS showed $[M-H]^-$ at *m/z* 433, corresponding to the molecular formula of $C_{26}H_{26}O_6$. The ^1H- and ^{13}C-NMR features of **51** ($CDCl_3$, Table 18) were similar to those of scandinone (**9**). The significant differences were the absence of the olefinic proton at the position H-2 and the presence of an ester carbonyl at δ 163.0 (C-2). From the spectroscopic data, compound **51** was therefore concluded to be scandenin. This compound was identified by comparison of spectroscopic data with the literature values.[20]

Chemical Modification

Lupalbigenin (**8**), the major component of the ethyl acetate extract, and derrisisoflavone A (**1**) and osajin (**44**), the minor components of the ethyl acetate extract, were subjected to structural modification. The synthezied analogues included derrisisoflvone A 7-*O*-acetate (**124**), derrisisoflavone A 4′-*O*-acetate (**125**), derrisisoflavone A 7,4′-di-*O*-acetate (**126**), lupalbigenin 7-*O*-acetate (**127**), lupalbigenin 4′-*O*-acetate (**128**), lupalbigenin 7,4′-di-*O*-acetate (**129**), osajin 4′-*O*-acetate (**130**), derrisisoflavone A 7-*O*-methyl ether (**131**), derrisisoflavone A 4′-*O*-methyl ether (**132**), derrisisoflavone A 7,4′-di-*O*-methyl ether (**133**), lupalbigenin 7-*O*-methyl ether (**134**), lupalbigenin 7,4′-di-*O*-methyl ether (**135**), 4′-*O*-methylosajin (**43**), tetrahydroderrisisoflavone A (**136**), hexahydroderrisisoflavone A (**137**), dihydrolupalbigenin (**138**), tetrahydrolupalbigenin (**139**), hexahydrolupalbigenin (**140**), tetrahydroosajin (**141**), hexahydroosajin (**142**), tetrahydrolupalbigenin 7-*O*-methyl ether (**143**), derrisisoflavone A 7-*O*-propanoate (**144**), derrisisoflavone A 4′-*O*-propanoate (**145**), derrisisoflavone A 7,4′-di-*O*-propanoate (**146**), 5′-nitrolupalbigenin (**147**), 2‴,3‴-epoxylupalbigenin (**148**), 2″,3″,2‴,3‴-diepoxylupalbigenin (**149**), lupalbigenin 7-*O*-benzoate (**150**), lupalbigenin 7,4′-di-*O*-benzoate (**151**), 7-*O*-propargyllupalbigenin (**152**), 7,4′-di-*O*-propargyllupalbigenin (**153**) and 7-*O*-[1⁗-(carboxymethyl)-1⁗,*H*-3⁗,4⁗,5⁗-triazole]lupalbigenin (**155**).

Acetylation of Derrisisoflavone A (1)



124; R_1 = Ac, R_2 = H

125; R_1 = H, R_2 = Ac

126; R_1 = R_2 = Ac

In order to synthesize acetate analogues of derrisisoflavone A (**1**) for biological evaluation, compound **1** was reacted with acetic anhydride in pyridine at room temperature to give derrisisoflavone A 7-*O*-acetate (**124**), derrisisoflavone A 4′-*O*-acetate (**125**) and derrisisoflavone A 7,4′-di-*O*-acetate (**126**) in 14, 3 and 44% yields, respectively.

Compound **124** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3176 cm^{-1}), acetate ester group (1767 cm^{-1}), conjugated ketone group (1625 cm^{-1}) and aromatic nucleus (1610, 1584 and 1515 cm^{-1}). The HR-TOFMS (positive ion electrospray, ESI^+) showed $[M+Na]^+$ at *m/z* 485.1931, corresponding to the molecular formula of $C_{28}H_{30}O_6$. The ^{1}H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 19) of compound **124** were similar to that of compound **1**. Comparison of ^{1}H-NMR spectrum of **124** with that of **1** indicated that the significant differences were the presence of acetyl signal at δ 2.33 (3H, *s*, 7-OAc) and the down-field shift of C-6 and C-8 signals at δ 126.1 and 119.7, respectively, and up-field

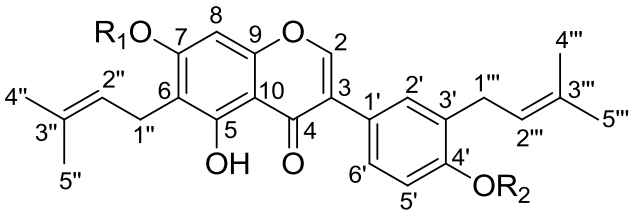
shift of the C-7 signal at δ 151.7. On the basis of the above data, the structure **124** was concluded as derrisisoflavone A 7-*O*-acetate.

Compound **125** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3319 cm^{-1}), acetate ester group (1760 cm^{-1}), conjugated carbonyl group (1633 cm^{-1}) and aromatic nucleus (1585 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 485.1933, corresponding to the molecular formula of $C_{28}H_{30}O_6$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 19) of compound **125** were similar to that of compound **1**. Comparison of ^1H-NMR spectrum of **125** with that of **1** indicated that the significant differences were the presence of acetyl signal at δ 2.29 (3H, *s*, 4′-OAc) and the down-field shift of H-2′, 6′ (δ 7.55), H-3′, 5′ (δ 7.12), C-3′, 5′ (δ 121.5) and up-field shift of C-4′ at δ 150.4. On the basis of the above data, the structure **125** was concluded as derrisisoflavone A 4′-*O*-acetate.

Compound **126** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of acetate ester group (1766 and 1754cm^{-1}), conjugated carbonyl group (1644 cm^{-1}) and aromatic nucleus (1586 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 527.2039, corresponding to the molecular formula of $C_{30}H_{32}O_7$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 20) of compound **126** were similar to that of compound **1**. Comparison of ^1H-NMR spectrum of **126** with that of **1** indicated that the significant differences were the presence of acetyl signals at δ 2.32 (3H, *s*, 7-OAc) and δ 2.91 (3H, *s*, 4′-OAc) which indicated the presence of two acetyl groups and the down-field shift of H-2′, 6′ (δ 7.54), H-3′, 5′ (δ 7.13) C-6 (δ 126.2), C-8 (δ

119.7) and C-3′, 5′ (δ 121.6) and up-field shift of C-7 and C-4′ at δ 151.8 and 150.6 , respectively. On the basis of the above data, the structure **126** was concluded as derrisisoflavone A 7,4′-di-*O*-acetate.

Acetylation of Lupalbigenin (8)



127; R_1 = Ac, R_2 = H

128; R_1 = H, R_2 = Ac

129; R_1 = R_2 = Ac

In order to synthesize acetate analogues of lupalbigenin (**8**) for biological evaluation, compound **8** was reacted with acetic anhydride in pyridine at room temperature to give lupalbigenin 7-*O*-acetate (**127**), lupalbigenin 4′-*O*-acetate (**128**) and lupalbigenin 7,4′-di-*O*-acetate (**129**) in 33, 10 and 57% yields, respectively.

Compound **127** was obtained as white amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3488 cm^{-1}), acetate ester group (1734 cm^{-1}), conjugated carbonyl group (1621 cm^{-1}) and aromatic nucleus (1592 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 471.1776, corresponding to the molecular formula of $C_{27}H_{28}O_6$. The ^{1}H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 21) of compound **127** were similar to that of compound **8**. Comparison of ^{1}H-NMR spectrum of **127** with that of **8** indicated that the significant differences were the presence of acetyl signal at δ 2.33 (3H, *s*, 7-OAc) and the down-field shift of H-8 (δ 6.69), C-6 (δ 117.3)

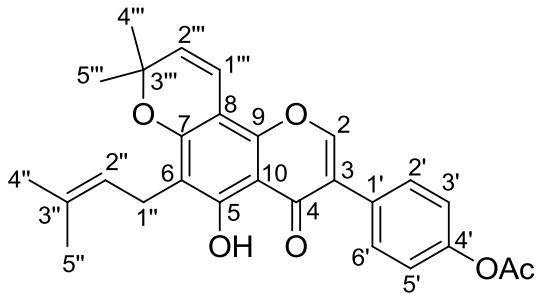
and C-8 (δ 101.1) and the up-field of C-7 at δ 154.1. On the basis of the above data, the structure **127** was concluded as lupalbigenin 7-*O*-acetate.

Compound **128** was obtained as white amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3193 cm^{-1}), acetate ester group (1733 cm^{-1}), conjugated carbonyl group (1642 cm^{-1}) and aromatic nucleus (1618 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 471.1767, corresponding to the molecular formula of $C_{27}H_{28}O_6$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 21) of compound **128** were similar to that of compound **8**. Comparison of ^1H-NMR spectrum of **128** with that of **8** indicated that the significant differences were the presence of acetyl signal at δ 2.31 (3H, *s*, 4′-OAc) and the down-field shift of H-2′ (δ 7.34), H-5′ (δ 7.06), H-6′ (δ 7.35), C-3′ (δ 133.4) and C-5′ (δ 122.5) and the up-field shift of C-4′ at δ149.0. On the basis of the above data, the structure **128** was concluded as lupalbigenin 4′-*O*-acetate.

Compound **129** was obtained as white amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3081 cm^{-1}), acetate ester group (1748 cm^{-1}), conjugated carbonyl group (1626 cm^{-1}) and aromatic nucleus (1593 cm^{-1}). The HR-TOFMS (positive ion electrospray, ESI^+) showed $[M+Na]^+$ at *m/z* 513.1879, corresponding to the molecular formula of $C_{29}H_{30}O_7$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 22) of compound **129** were similar to that of compound **8**. Comparison of ^1H-NMR spectrum of **129** with that of **8** indicated that the significant differences were the presence of acetyl signals at δ 2.33 (3H, *s*, 7-OAc) and δ 2.31 (3H, *s*, 4′-OAc) which indicated the presence of two acetyl groups and the down-field

shift of H-8 (δ 6.71), H-2′ (δ 7.34), H-5′ (δ 7.08), H-6′ (δ 7.35), C-6 (δ 117.5), C-8 (δ 101.2), C-3′ (δ 133.9) and C-5′ (δ 122.5) and the up-field shift of C-7 and C-4′ signals at δ 154.6 and 149.1, respectively. On the basis of the above data, the structure **129** was concluded as lupalbigenin 7,4′-di-*O*-acetate.

Acetylation of Osajin (44)



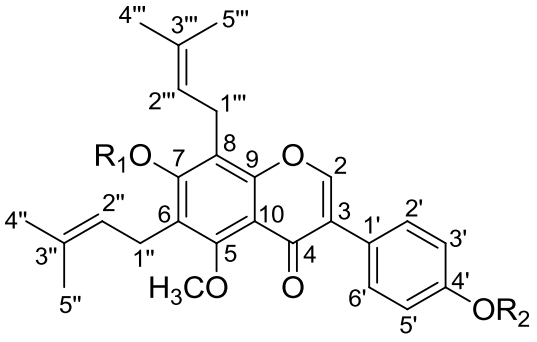
(130)

In order to synthesize acetate analogue **130** of osajin (**44**) for biological evaluation, compound **44** was reacted with acetic anhydride in pyridine at room temperature to give osajin 4′-*O*-acetate (**130**) in 95% yield.

Compound **130** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3341 cm^{-1}), acetate ester group (1750 cm^{-1}), conjugated carbonyl group (1651 cm^{-1}) and aromatic nucleus (1615, 1573 and 1508 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 469.1633, corresponding to the molecular formula of $C_{27}H_{26}O_6$. The ^{1}H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 23) of compound **130** were similar to that of compound **44**. Comparison of ^{1}H-NMR spectrum of **130** with that of **44** indicated that the significant differences were

the presence of acetyl signal at δ 2.30 (3H, *s*, 4′-OAc) and the down-field shift of H-2′, 6′ (δ 7.53), H-3′, 5′ (δ 7.15) and C-3′, 5′ (δ 121.8) and the up-field shift of C-4′ signal at δ 150.7. On the basis of the above data, the structure **130** was concluded as osajin 4′-*O*-acetate.

Methylation of Derrisisoflavone A (1)



131; $R_1 = CH_3$, $R_2 = H$

132; $R_1 = H$, $R_2 = CH_3$

133; $R_1 = R_2 = CH_3$

In order to synthesize methyl ether analogues of derrisisoflavone A (**1**) for biological evaluation, compound **1** was reacted with methyl iodide and sodium carbonate in acetone at 40^{o}C to give derrisisoflavone A 7-*O*-methyl ether (**131**), derrisisoflavone A 4′-*O*-methyl ether (**132**) and derrisisoflavone A 7,4′-di-*O*-methyl ether (**133**) in 34, 18 and 19% yields, respectively.

Compound **131** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3362 cm^{-1}), conjugated carbonyl group (1634 cm^{-1}) and aromatic nucleus (1608, 1587 and 1516 cm^{-1}). The HR-TOFMS (ESI^{+}) spectrum, which showed $[M+Na]^{+}$ at *m/z* 457.1959, corresponding to the molecular formula of $C_{27}H_{30}O_5$. The ^{1}H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 24) of compound **131** were similar to that of

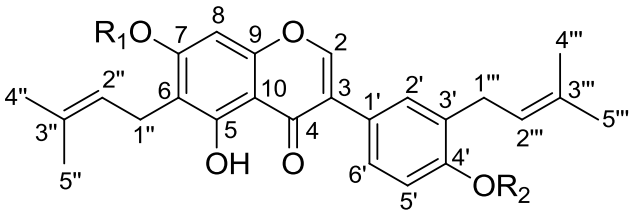
compound **1**. Comparison of ^{1}H-NMR spectrum of **131** with that of **1** indicated that the significant differences were the presence of methoxyl signal at δ 3.84 (3H, *s*, 7-OCH_3) and the down-field shift of C-6 and C-8 signals at δ 127.1 and 119.9, respectively, and up-field shift of the C-7 signal at δ 156.9. On the basis of the above data, the structure **131** was concluded as derrissioflavone A 7-*O*-methyl ether.

Compound **132** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3344 cm^{-1}), conjugated carbonyl group (1633 cm^{-1}) and aromatic nucleus (1607, 1587 and 1512 cm^{-1}). The HR-TOFMS (ESI^{+}) showed $[M+Na]^{+}$ at *m/z* 457.1961, corresponding to the molecular formula of $C_{27}H_{30}O_5$. The ^{1}H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 24) of compound **132** were similar to that of compound **1**. Comparison of ^{1}H-NMR spectrum of **132** with that of **1** indicated that the significant differences were the presence of methoxyl signal at δ 3.80 (3H, *s*, 4′-OCH_3) and the down-field shift of H-2′, 6′ (δ 7.45), H-3′, 5′ (δ 6.94) and C-4′ (δ 159.4). On the basis of the above data, the structure **132** was concluded as derrissioflavone A 4′-*O*-methyl ether.

Compound **133** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of conjugated carbonyl group (1638 cm^{-1}) and aromatic nucleus (1608, 1582 and 1512 cm^{-1}). The HR-TOFMS (ESI^{+}) showed $[M+Na]^{+}$ at *m/z* 471.2113, corresponding to the molecular formula of $C_{28}H_{32}O_5$. The ^{1}H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 25) of compound **133** were similar to that of compound **1**. Comparison of ^{1}H-NMR spectrum of **133** with that of **1** indicated that the significant differences were

the presence of methoxyl signals at δ 3.78 (3H, *s*, 7-OCH_3) and δ 3.81 (3H, *s*, 4′-OCH_3) which indicated the presence of two methoxyl groups and the down-field shift of H-2′, 6′ (δ 7.45), H-3′, 5′ (δ 6.94), C-6 (δ 126.3), C-7 (δ 161.0), C-8 (δ 119.8) and C-4′ (δ 159.5). On the basis of the above data, the structure **133** was concluded as derrissioflavone A 7,4′-di-*O*-methyl ether.

Methylation of Lupalbigenin (8)



134; $R_1 = CH_3$, $R_2 = H$

135; $R_1 = R_2 = CH_3$

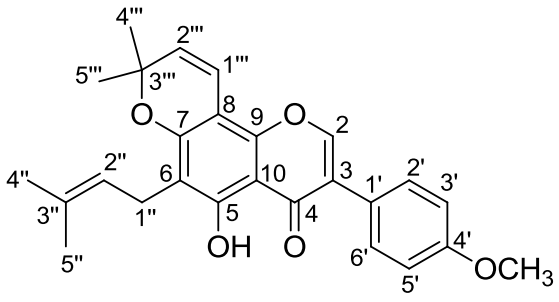
In order to synthesize methyl ether analogues of lupalbigenin (**8**) for biological evaluation, compound **8** was reacted with methyl iodide and sodium carbonate in acetone at 40^{o}C to give lupalbigenin 7-*O*-methyl ether (**134**) and lupalbigenin 7,4′-di-*O*-methyl ether (**135**) in 71 and 26% yields, respectively.

Compound **134** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3326 cm^{-1}), conjugated carbonyl group (1649 cm^{-1}) and aromatic nucleus (1613 and 1573 cm^{-1}). The HR-TOFMS (ESI^{+}) showed $[M+Na]^{+}$ at *m/z* 443.1808, corresponding to the molecular formula of $C_{26}H_{28}O_5$. The ^{1}H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 26) of compound **134** were similar to that of compound **8**. Comparison of ^{1}H-NMR spectrum of **134** with that of **8** indicated that the significant

differences were the presence of methoxyl signal at δ 3.87 (3H, *s*, 7-OCH_3) and the down-field shift of C-6 (δ 113.0) and C-7 (δ 163.2) and the up-field shift of C-8 signal at δ 89.4. On the basis of the above data, the structure **134** was concluded as lupalbigenin 7-*O*-methyl ether.

Compound **135** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3347 cm^{-1}), conjugated carbonyl group (1644 cm^{-1}) and aromatic nucleus (1608, 1568 and 1501 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 457.1983, corresponding to the molecular formula of $C_{27}H_{30}O_5$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 26) of compound **135** were similar to that of compound **8**. Comparison of ^1H-NMR spectrum of **135** with that of **8** indicated that the significant differences were the presence of methoxyl signals at δ 3.88 (3H, s, 7,-OCH_3) and δ 3.84 (3H, s, 4′-OCH_3) which indicated the presence of two methoxyl groups and the down-field shift of H-6′ (δ 7.33), C-6 (δ 113.0), C-7 (δ 163.2), C-3′ (δ 130.4), C-4′ (δ 157.5) and the up-field shift of C-8 and C-5′ signals at δ 89.4 and 110.3, respectively. On the basis of the above data, the structure **135** was concluded as lupalbigenin 7,4′-di-*O*-methyl ether.

Methylation of Osajin (44)

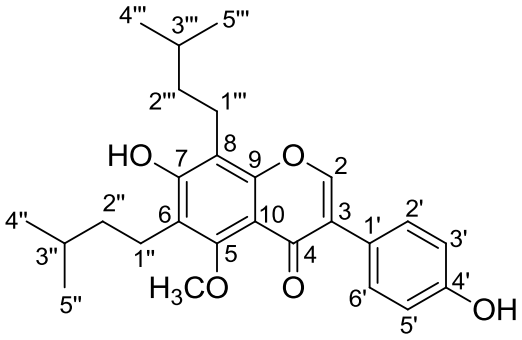


(43)

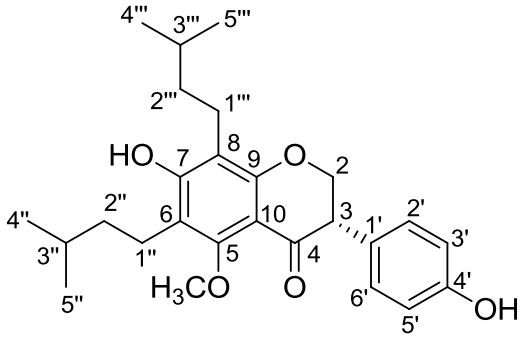
In order to synthesize methyl ether analogues **43** of osajin (**44**) for biological evaluation, compound **44** was reacted with methyl iodide and sodium carbonate in acetone at 40^{o}C to give 4′-*O*-methylosajin (**43**) in 84% yield.[21]

Compound **43** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3321 cm^{-1}), conjugated carbonyl group (1650 cm^{-1}) and aromatic nucleus (1614, 1567 and 1510 cm^{-1}). The HR-TOFMS (ESI^{+}) showed [M+Na]$^{+}$ at *m/z* 441.1645, corresponding to the molecular formula of $C_{26}H_{26}O_5$. The ^{1}H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 16) of compound **43** were similar to that of compound **44**. Comparison of ^{1}H-NMR spectrum of **43** with that of **44** indicated that the significant differences were the presence of methoxyl signal at δ 3.82 (3H, *s*, 4′-OCH_3) and the down-field shift of H-2′, 6′ (δ 7.44), H-3′, 5′ (δ 6.96) and C-4′ (δ 159.7). On the basis of the above data, the structure **43** was concluded as 4′-*O*-methylosajin.

Catalytic of Hydrogenation of Derrisisoflavone A (1)



(**136**)



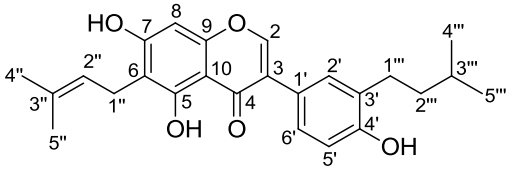
(**137**)

Hydrogenation of derrisisoflavone A (**1**) with 10% Pd-C in EtOH as a catalyst at atmospheric pressure gave tetrahydro analogue **136** and the hexahydro analogue **137** in 49 and 45 % yields, respectively.

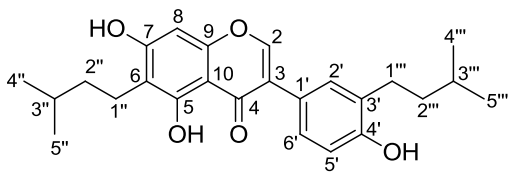
Compound **136** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3173 cm^{-1}), conjugated carbonyl group (1631 cm^{-1}) and aromatic nucleus (1607, 1586 and 1516 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 447.2145, corresponding to the molecular formula of $C_{26}H_{32}O_5$. The ^1H- and ^{13}C-NMR spectrum ($CDCl_3$ + 2 drops of CD_3OD, Table 27) of compound **136** were similar to that of derrisisoflavone A (**1**). The prenyl group were converted into isopeutyl group and the presence of aliphatic proton signals at δ 1.36-1.44 (2×2H, *m*, H-2″, H-2‴), 1.58-1.65 (2×1H, *m*, H-3″, H-3‴), 2.67 (2H, *dd*, *J* = 8.2, 3.0 Hz, H-1″) and 2.75 (2H, *dd*, *J* = 8.0, 2.7 Hz, H-1‴). On the basis of the above data, the structure **136** was concluded as tetrahydroderrisisoflavone A.

Compound **137** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3339 cm^{-1}) and aromatic nucleus (1581 and 1517 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 449.2294, corresponding to the molecular formula of $C_{26}H_{34}O_5$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$ + 2 drops of CD_3OD, Table 27) of compound **137** were similar to that of tetrahydroderrisisoflavone A (**136**). The significant differences were the absence of the olefinic signal of H-2 and the presence of aliphatic protons at δ 4.51 (1H, *dd*, *J* = 11.2, 5.2 Hz, H-2*β*), 4.49 (1H, *dd*, *J* = 11.2, 9.0 Hz, H-2*α*) and 3.68 (1H, *br dd*, *J* = 9.0, 5.2 Hz, H-3). On the basis of the above data, the structure of **137** was concluded as hexahydroderrisisoflavone A.

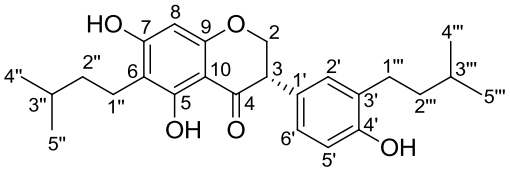
Catalytic of Hydrogenation of Lupalbigenin (8)



(**138**)



(**139**)



(**140**)

Hydrogenation of lupalbigenin (**8**) with 10% Pd-C in EtOH as a catalyst at atmospheric pressure gave the dihydro analogue **138**, tetrahydro analogue **139** and hexahydro analoge **140** in 9, 47 and 26 % yields, respectively.

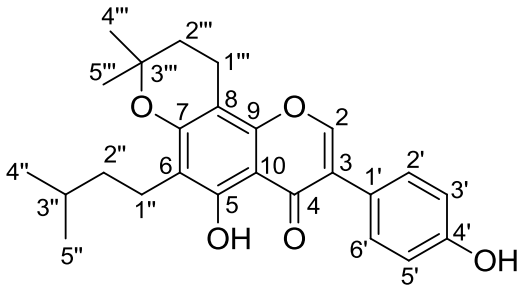
Compound **138** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3263 cm^{-1}), conjugated carbonyl group (1651 cm^{-1}) and aromatic nucleus (1616, 1552 and 1506 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 431.1829, corresponding to the molecular formula of $C_{32}H_{36}O_7$. The ^1H- and ^{13}C-NMR spectra ($CDCl_3$, Table 28) of compound **138** were similar to those of lupalbigenin (**8**). The prenyl group were converted into isopeutyl group and the presence of aliphatic proton signals at δ 1.47-1.53 (2H, *m*, H-2‴), 1.55-1.65 (1H, *m*, H-

3′′′) and δ 2.61 (2H, *t*, *J* = 8.2 Hz, H-1′′′). On the basis of the above data, the structure **138** was concluded as dihydrolupalbegenin.

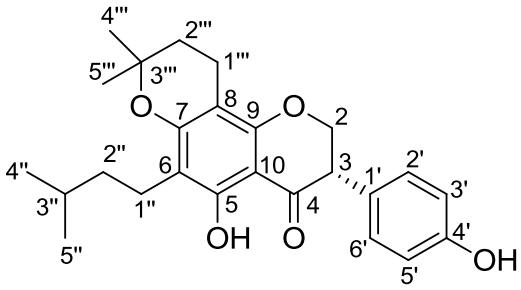
Compound **139** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3261 cm^{-1}), conjugated carbonyl group (1651 cm^{-1}) and aromatic nucleus (1620, 1609 and 1560 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 433.1947, corresponding to the molecular formula of $C_{25}H_{30}O_5$. The ^1H- and ^{13}C-NMR spectra ($CDCl_3$, Table 28) of compound **139** were similar to those of lupalbigenin (**8**). The prenyl group were converted into isopeutyl group and the presence of aliphatic proton signals at δ 1.36-1.40 (2H, *m*, H-2′′), 1.44-1.50 (2H, *m*, H-2′′′), 1.52-1.63 (2×1H, *m*, H-3′′, H-3′′′), 2.63 (2H, *dd*, *J* = 7.9, 2.4 Hz, H-1′′) and 2.59 (2H, *dd*, *J* = 8.2, 2.4 Hz, H-1′′′). On the basis of the above data, the structure of **139** was concluded as tetrahydrolupalbigenin.

Compound **140** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3254 cm^{-1}) and aromatic nucleus (1616, 1551 and 1504 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 435.2145, corresponding to the molecular formula of $C_{25}H_{32}O_5$. The ^1H- and ^{13}C-NMR spectrum ($CDCl_3$, Table 29) of compound **140** were similar to that of tetrahydrolupalbigenin (**139**). The significant differences were the absence of the olefinic signal of H-2 and the presence of aliphatic proton signals at δ 4.52 (1H, *dd*, *J* = 11.0, 5.3 Hz, H-2*β*), 4.47 (1H, *dd*, *J* = 11.0, 9.3 Hz, H-2*α*) and δ 3.85 (1H, *dd*, *J* = 9.3, 5.3 Hz, H-3). On the basis of the above data, the structure of **140** was concluded as hexahydrolupalbigenin.

Catalytic of Hydrogenation of Osajin (44)



(**141**)



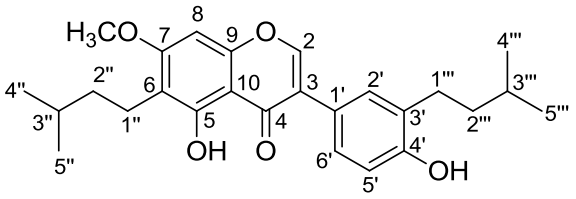
(**142**)

Hydrogenation of osajin (**44**) with 10% Pd-C in EtOH as a catalyst at atmospheric pressure gave the tetrahydro analogue **141** and hexahydro analogue **142** in 46 and 41 % yields, respectively.

Compound **141** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3375 cm^{-1}), conjugated carbonyl group (1643 cm^{-1}) and aromatic nucleus (1611, 1569 and 1515 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 431.1798, corresponding to the molecular formula of $C_{25}H_{28}O_5$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 30) of compound **141** were similar to those of compound **44**. The prenyl group and pyran group were converted into isopeutyl group and dihydropyran group and the presence of aliphatic proton signals at δ 1.30-1.39 (2H, partially overlapping signals, H-2″) and 1.51-1.60 (1H, *m*, H-3″), 2.68 (2H, *br t*, *J* = 7.9 Hz, H-1″), 2.72 (2H, *t*, *J* = 6.8 Hz, H-1‴) and 1.80 (2H, *t*, *J* = 6.8 Hz, H-2‴). On the basis of the above data, the structure of **141** was concluded as tetrahydroosajin.

Compound **142** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3431 cm^{-1}) and aromatic nucleus (1604, 1589 and 1519 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 433.1983, corresponding to the molecular formula of $C_{25}H_{30}O_5$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 30) of compound **142** were similar to those of compound **141**. The significant differences were the absence of the olefinic signal of H-2 and the presence of aliphatic proton signals at δ 4.52 (1H, *dd*, *J* = 11.3, 5.0 Hz, H-2*β*), 4.43 (1H, *dd*, *J* = 11.3, 8.5 Hz, H-2*α*) and δ 3.84 (1H, *dd*, *J* = 8.5, 5.0 Hz, H-3). The *4′*-hydroxyphenyl group at C-3 was in the more stable equatorial orientation. On the basis of the above data, the structure of **142** was concluded as hexahydroosajin.

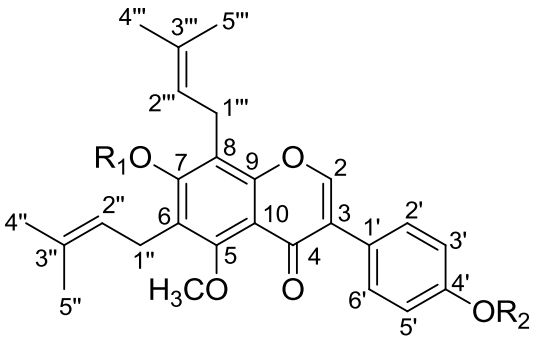
Catalytic of Hydrogenation of Lupalbigenin 7-*O*-methyl ether (134)



(**143**)

Hydrogenation of lupalbigenin 7-*O*-methyl ether (**134**) with 10% Pd-C in EtOH as a catalyst at atmospheric pressure gave the tetrahydro analogue **143** in 29% yield. Compound **143** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3382 cm^{-1}), conjugated carbonyl group (1649 cm^{-1}) and aromatic nucleus (1614, 1572 and 1506 cm^{-1}). The HR-TOFMS (ESI^{+}) spectrum, which showed $[M+Na]^{+}$ at *m/z* 447.2138, corresponding to the molecular formula of $C_{26}H_{32}O_5$. The ^{1}H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 31) of compound **143** were similar to those of compound **139**. The significant difference was the presence of methoxyl signal at δ 3.83 (3H, *s*, 7-OCH_3). On the basis of the above data, the structure of **143** was concluded as tetrahydrolupalbigenin 7-*O*-methyl ether.

Esterification of Derrisisoflavone A (1) with Propionic anhydride



144; $R_1 = COCH_2CH_3$, $R_2 = H$

145; $R_1 = H$, $R_2 = COCH_2CH_3$

146; $R_1 = R_2 = COCH_2CH_3$

Reaction of derrisisoflavone A (**1**) with propionic anhydride and pyridine in dichloromethane at room temperature gave derrisisoflavone A 7-*O*-propanoate (**144**), derrisisoflavone A 4′-*O*-propanoate (**145**) and derrisisoflavone A 7,4′-di-*O*-propanoate (**146**) in 14, 3 and 44% yields, respectively.

Compound **144** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3350 cm^{-1}), ester group (1758 cm^{-1}), conjugated carbonyl group (1630 cm^{-1}) and aromatic nucleus (1587 and 1512 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 499.2086, corresponding to the molecular formula of $C_{29}H_{32}O_6$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 32) of compound **144** were similar to those of compound **1**. The significant differences were the presence of methyl proton signal at δ 1.27 (3H, *t*, *J* = 7.6 Hz, 7-$COCH_2\underline{CH_3}$) and methylene proton signal at δ 2.63 (2H, *q*, *J* = 7.6 Hz, 7-$CO\underline{CH_2}CH_3$) and the down-field shift of C-8 signal at δ 115.5 and up-field shift of the C-7 signal at δ 151.8. On

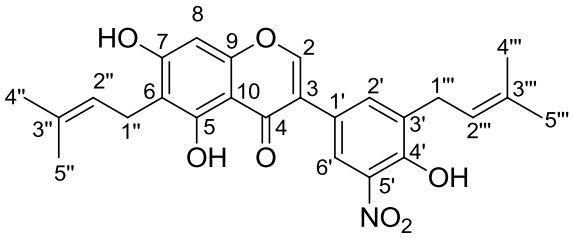
the basis of the above data, the structure of **144** was concluded as a derrisisoflavone A 7-*O*-propanoate.

Compound **145** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3316 cm^{-1}), ester group (1758 cm^{-1}), conjugated carbonyl group (1631 cm^{-1}) and aromatic nucleus (1583 and 1505 cm^{-1}). The HR-TOFMS (ESI^+) spectrum, which showed $[M+Na]^+$ at *m/z* 499.2090, corresponding to the molecular formula of $C_{29}H_{32}O_6$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 32) of compound **145** were similar to that of compound **1**. Comparison of ^1H-NMR spectrum of **145** with those of **1** indicated that the significant differences were the presence of methyl proton signal at δ 1.25 (3H, *t*, *J* = 7.5 Hz, 4′-$COCH_2\underline{CH_3}$), methylene proton signal at δ 2.58 (2H, *q*, *J* = 7.5 Hz, 4′-$CO\underline{CH_2}CH_3$) and the down-field shift of H-2′, 6′ (δ 7.54), H-3′, 5′ (δ 7.12) and C-3′, 5′ (δ 121.5) and the up-field shift of C-4′ at δ150.6. On the basis of the above data, the structure of **145** was concluded as a derrisisoflavone A 4′-*O*-propanoate.

Compound **146** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of ester group (1766 and 1746 cm^{-1}), conjugated carbonyl group (1644 cm^{-1}) and aromatic nucleus (1588 cm^{-1}). The HR-TOFMS (ESI^+) spectrum, which showed $[M+Na]^+$ at *m/z* 555.2357, corresponding to the molecular formula of $C_{32}H_{36}O_7$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 33) of compound **146** were similar to that of compound **1**. Comparison of ^1H-NMR spectrum of **146** with that of **1** indicated that the significant differences were the presence of methyl proton

signals at δ 1.25 (3H, *t*, *J* = 7.4 Hz, 4′-COCH$_2$CH$_3$), δ 1.27 (3H, *t*, *J* = 7.4 Hz, 7-COCH$_2$CH$_3$), methylene proton signals at δ 2.56 (2H, *q*, *J* = 7.4 Hz, 4′-COCH$_2$CH$_3$), δ 2.62 (2H, *q*, *J* = 7.4 Hz, 7-COCH$_2$CH$_3$) and the down-field shift of H-2′, 6′ (δ 7.54), H-3′, 5′ (δ 7.13), C-6 (δ 126.3), C-8 (δ 119.8) and C-3′, 5′ (δ 121.6) and the up-field shift of C-7 and C-4′ at δ 151.9 and 150.7, respectively. On the basis of the above data, the structure of **146** was concluded as a derrisisoflavone A 7,4′-di-*O*-propanoate.

Nitration of Lupalbigenin (8)

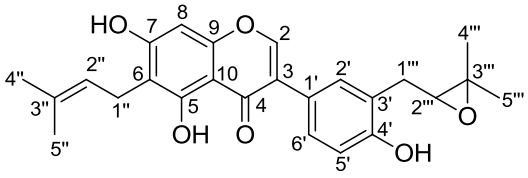


(**147**)

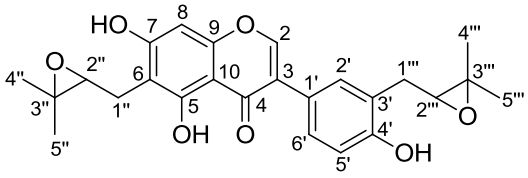
Reaction of lupalbigenin (**8**) with $NaNO_2$ in the presence H_2SO_4 in methanol gave 5′-nitrolupalbigenin (**147**) in 22% yield. Compound **147** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3355 cm^{-1}), conjugated carbonyl group (1644 cm^{-1}), aromatic nucleus (1623 and 1544 cm^{-1}) and nitro group (1571 and 1367 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 474.1485, corresponding to the molecular formula of $C_{25}H_{25}NO_7$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 34) of compound **147** were similar to those of compound **8**.

The significant differences were the presence of chelated hydroxyl group at δ 10.96 (1H, *s,* 4′-OH) and the down-field shift of the H-2′ (δ 7.58), H-6′ (δ 8.07), C-2′ (δ 137.7), C-3′ (δ 133.7) and C-5′ (δ 133.1) and the up-field shift of C-6′ signal at δ 7.58. On the basis of the above data, the structure of **147** was concluded as 5′-nitrolupalbigenin.

Epoxidation of Lupalbigenin (8)



(**148**)



(**149**)

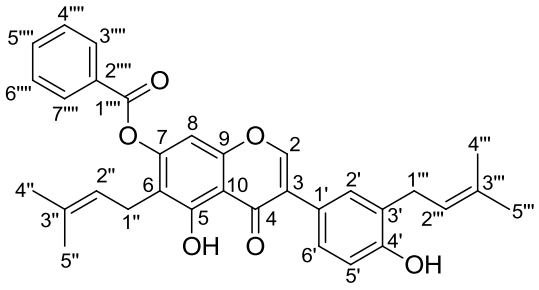
In order to synthesize epoxide analogues of lupalbigenin (**8**) for biological evaluation, compound **8** was reacted with *meta*-chloroperbenzoic acid (*m*-CPBA) in chlorofrom at room temperature to give 2‴,3‴-epoxylupalbigenin (**148**) and 2″,3″,2‴,3‴-diepoxylupalbigenin (**149**) in 5 and 13% yields, respectively.

Compound **148** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3242 cm^{-1}), conjugated carbonyl group (1645 cm^{-1}) and aromatic nucleus (1614 and 1578 cm^{-1}). The HR-TOFMS (ESI^+) spectrum, which showed $[M+Na]^+$ at *m/z* 445.1618, corresponding to the molecular formula of $C_{25}H_{26}O_6$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 35) of compound **148** were similar to that of

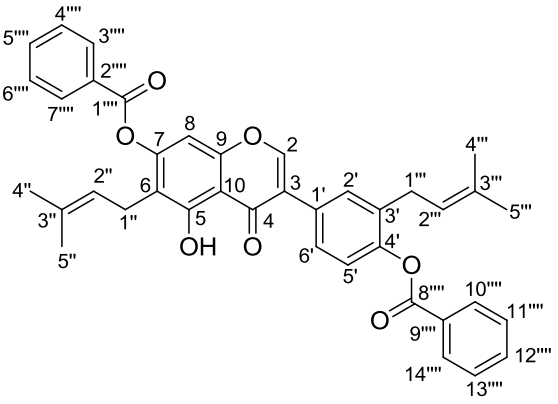
compound **8**. The significant differences were the absence of the olefinic signals and the presence methine proton signal at δ 3.81 (1H, *br dd*, 5.7, 4.5 Hz, H-2‴, the methylene proton signals at δ 2.81 (1H, *dd*, *J* = 16.9, 5.7 Hz, H-1‴a) and 3.11 (1H, *dd*, *J* = 16.9, 4.5 Hz, H-1‴b). On the basis of the above data, the structure of **148** was concluded as 2‴,3‴-expoylupalbigenin.

Compound **149** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3389 cm^{-1}), conjugated carbonyl group (1651 cm^{-1}) and aromatic nucleus (1614 and 1567 cm^{-1}). The HR-TOFMS (ESI^+) spectrum, which showed $[M+Na]^+$ at *m/z* 461.1575, corresponding to the molecular formula of $C_{25}H_{26}O_7$. The ^1H- and ^{13}C-NMR spectral data (CD_3OD, Table 35) of compound **149** were similar to those of compound **8**. The significant differences were the absence of two olefinic signals and the presence methine proton signals at δ 3.84 (1H, *dd*, *J* = 5.9, 5.1 Hz, H-2″) and 3.79 (1H, *dd*, *J* = 5.6, 4.8 Hz, H-2‴), the methylene proton signals at δ 2.95 (1H, *dd*, *J* = 17.2, 5.1 Hz, H-1″b), 2.71 (1H, *dd*, *J* = 17.2, 5.9 Hz, H-1″a), 3.09 (1H, *dd*, *J* = 16.8, 4.8 Hz, H-1‴b) and 2.80 (1H, *dd*, *J* = 16.8, 5.6 Hz, H-1‴a). On the basis of the above data, the structure of **149** was concluded as 2″,3″,2‴,3‴-diexpoylupalbigenin.

Benzoylation of Lupalbigenin (8)



(**150**)



(**151**)

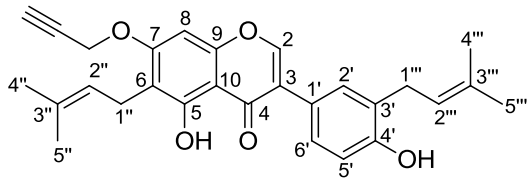
In order to synthesize benzoate analogues of lupalbigenin (**8**) for biological evaluation, compound **8** was reacted with benzoyl chloride and pyridine in dichlorometane at room temperature to give lupalbigenin 7-*O*-benzoate (**150**) and lupalbigenin 7,4′-di-*O*-benzoate (**151**) in 7 and 52% yields, respectively.

Compound **150** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3452 cm^{-1}), benzoate carbonyl ester group (1717 cm^{-1}), conjugated carbonyl group (1641 cm^{-1}) and aromatic nucleus (1617, 1578 and 1509 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 533.1941, corresponding to the molecular formula of $C_{32}H_{30}O_6$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 36) of compound **150** were similar to that of compound **8**. Comparison of ^1H-NMR spectrum of **150** with that of **8** indicated that the significant differences were the presence of aromatic signals at δ 8.19 (2H, *d*, *J* = 7.7 Hz, H-3′′′′,7′′′′), 7.52

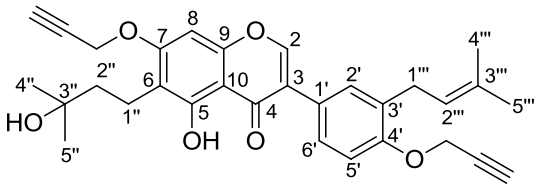
(2H, *t*, *J* = 7.7 Hz, H-4′′′′,6′′′′) and 7.66 (1H, *t*, *J* = 7.7 Hz, H-5′′′′), the down-field shift of H-8 (δ 6.81), C-6 (δ 117.6) and C-8 (δ 101.3) and the up-field shift of C-7 signal at δ 154.8. On the basis of the above data, the structure **150** was concluded as lupalbigenin 7-*O*-benzoate.

Compound **151** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3062 cm^{-1}), benzoate carbonyl ester group (1750 and 1733 cm^{-1}), conjugated carbonyl group (1645 cm^{-1}) and aromatic nucleus (1619, 1582 and 1512 cm^{-1}). The HR-TOFMS (ESI^+) spectrum, which showed $[M+Na]^+$ at *m/z* 637.2205, corresponding to the molecular formula of $C_{31}H_{30}O_5$. The ^{1}H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 36) of compound **151** were similar to that of compound **8**. Comparison of ^{1}H-NMR spectrum of **151** with those of **8** indicated that the significant differences were the presence of aromatic signals at δ 8.19-8.21 (4H, overlapping signal, H-3′′′′, 7′′′′, 10′′′′, 14′′′′), 7.54 (2H, *t*, *J* = 7.8 Hz, H-4′′′′,6′′′′), 7.66 (1H, *t*, *J* = 7.8 Hz, H-5′′′′), 7.52 (2H, *t*, *J* = 7.9 Hz, H-11′′′′,13′′′′) and 7.64 (1H, *t*, *J* = 7.9 Hz, H-12′′′′), the down-field shift of H-8 (δ 6.85), H-2′ (δ 7.42), H-5′ (δ 7.23), H-6′ (δ 7.43), C-6 (δ 117.8), C-8 (δ 101.4), C-3′ (δ 133.5), C-5′ (δ 122.7) and the up-field shift of C-7 and C-4′ signals at δ 154.7 and 149.4, respectively. On the basis of the above data, the structure of **151** was concluded as lupalbigenin 7,4′-di-*O*-benzoate.

Reaction of Lupalbigenin (8) with Propargyl Bromide



(**152**)



(**153**)

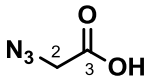
Reaction of lupalbigenin (**8**) with potassium carbonate and propargyl bromide in acetone gave 7-*O*-propargyllupalbigenin (**152**) and lupalbigenin 7,4′-di-*O*-dipropargyllupalbigenin (**153**) in 72 and 21% yields, respectively.

Compound **152** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3284 cm^{-1}), alkyne group (2126 cm^{-1}), conjugated carbonyl group (1647 cm^{-1}) and aromatic nucleus (1614 cm^{-1}). The HR-TOFMS (ESI^+) showed $[M+Na]^+$ at *m/z* 467.1779, corresponding to the molecular formula of $C_{28}H_{28}O_5$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 37) of compound **152** was similar to those of compound **8**. The significant differences were the presence of methylene proton signals at δ 4.77 (2H, *d*, *J* = 2.4 Hz, 7-O$\underline{CH_2}$C≡CH), methine proton signal at δ 2.55 (1H, *t*, *J* = 2.4 Hz, 7-OCH$_2$C≡$\underline{CH}$), the down-field shift of the H-8 (δ 6.50) and C-6 (δ 113.5) and the up-field shift of C-7 and C-8 signals at δ 160.9 and 90.6, respectively. On the basis of the above data, the structure of **152** was concluded as 7-*O*-propargyllupalbigenin.

Compound **153** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3292 cm^{-1}), alkyne group

(2124 cm^{-1}), conjugated carbonyl group (1647 cm^{-1}) and aromatic nucleus (1618 and 1582 cm^{-1}). The HR-TOFMS (ESI^+) spectrum, which showed $[M+Na]^+$ at *m/z* 505.1914, corresponding to the molecular formula of $C_{31}H_{30}O_5$. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 37) of compound **153** were similar to those of compound **8**. The significant differences were the presence of methylene proton signals at δ 4.76 (2H, *d*, *J* = 2.4 Hz, 7-O$\underline{CH_2}$C≡CH) and 4.72 (2H, *d*, *J* = 2.4 Hz, 4′-O$\underline{CH_2}$C≡CH), methine proton signals at δ 2.55 (1H, *t*, *J* = 2.4 Hz, 7-OCH$_2$C≡$\underline{CH}$) and 2.50 (1H, *t*, *J* = 2.4 Hz, 4′-OCH$_2$C≡$\underline{CH}$), the down-field shift of H-8 (δ 6.49), H-5′ (δ 7.00), H-6′ (δ 7.32), C-6 (δ 113.6) and C-3′ (δ 131.1) and the up-field shift of C-7 (δ 161.0), C-8 (δ 90.7) and C-5′ (δ 111.9). On the basis of the above data, the structure of **153** was concluded as 7,4′-di-*O*-propargyllupalbigenin.

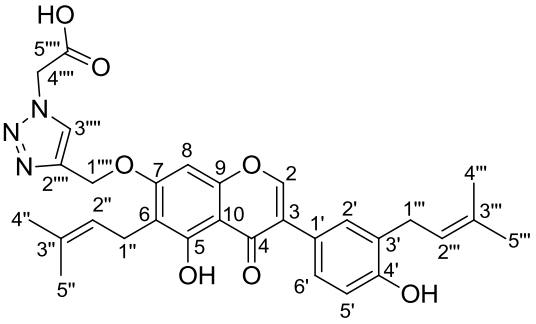
Synthesis of 2-Azidoacetic acid (154)



(**154**)

Reaction of bromoacetic acid with sodium azide in water gave 2-azidoacetic acid (**154**) in 94% yield.[22] Compound **154** was obtained as colorless liquid. The ^1H- and ^{13}C-NMR spectral data ($CDCl_3$, Table 38) of compound **154** showed a hydroxyl group at signal at δ 9.33 (1H, *s*, 3-OH) and methylene proton at δ 3.94 (2H, *s*, H-2). On the basis of the above data, the structure of **154** was concluded as 2-azidoacetic acid.

Click reaction of 7-*O*-Propargyllupalbigenin (152) with 2-Azidoacetic Acid (154)



(**155**)

Reaction of 7-*O*-propargylluaplbigenin (**152**) with 2-azidoacetic acid (**154**) in the presence of sodium ascorbate, $CuSO_4 \cdot 5H_2O$, in THF/H_2O gave **7-*O*-**[1′′′′-(carboxymethyl)-1′′′′,*H*-3′′′′,4′′′′,5′′′′-triazole]lupalbigenin (**155**) in 43% yield.

Compound **155** was obtained as yellow amorphous solid. The IR spectrum indicated the presence of hydroxyl group (3382 cm^{-1}) and aromatic nucleus (1614 and 1510 cm^{-1}). The HR-TOFMS (ESI^-) spectrum, which showed $[M-H]^-$ at *m/z* 544.2110, corresponding to the molecular formula of $C_{30}H_{31}N_3O_7$. The ^1H- and ^{13}C-NMR spectral data (CD_3OD, Table 39) of compound **155** were similar to that of compound **8**. The significant differences were the presence of triazole group at δ 8.09 (1H, *s*, H-3′′′′), the methylene proton signals at δ 5.32 (2H, *s*, H-1′′′′) and 5.02 (2H, *s*, H-4′′′′). The down-field shift of H-8 signal at δ 6.85 was observed and the down-field shift of C-6 and C-7 signal at δ 114.4 and 163.6, respectively. On the basis of

the above data, the structure of **155** was concluded as **7-***O*-[1‴-(carboxymethyl)-1‴,*H*-3‴,4‴,5‴-triazole]lupalbigenin.

Biological Activities

The biological activity of the natural compounds; derrisisoflavone A (**1**), 5,7,4′-trihydroxy-6,8-diprenylisoflavone (**7**), lupalbienin (**8**), scandinone (**9**), scanderone (**28**), osajin (**44**) and scandenin (**51**), and the synthetic analogues; derrisisoflvone A 7-*O*-acetate (**124**), derrisisoflavone A 4′-*O*-acetate (**125**), derrisisoflavone A 7,4′-di-*O*-acetate (**126**), lupalbigenin 7-*O*-acetate (**127**), lupalbigenin 4′-*O*-acetate (**128**), lupalbigenin 7,4′-di-*O*-acetate (**129**), osajin 4′-*O*-acetate (**130**), derrisisoflavone A 7-*O*-methyl ether (**131**), derrisisoflavone A 4′-*O*-methyl ether (**132**), derrisisoflavone A 7,4′-di-*O*-methyl ether (**133**), lupalbigenin 7-*O*-methyl ether (**134**), lupalbigenin 7,4′-di-*O*-methyl ether (**135**), 4′-*O*-methylosajin (**43**), tetrahydroderrisisoflavone A (**136**), hexahydroderrisisoflavone A (**137**), dihydrolupalbigenin (**138**), tetrahydrolupalbigenin (**139**), hexahydrolupalbigenin (**140**), tetrahydroosajin (**141**), hexahydroosajin (**142**), tetrahydrolupalbigenin 7-*O*-methyl ether (**143**), derrisisoflavone A 7-*O*-propanoate (**144**), derrisisoflavone A 4′-*O*-propanoate (**145**), derrisisoflavone A 7,4′-di-*O*-propanoate (**146**), 5′-nitrolupalbigenin (**147**), 2‴,3‴-epoxylupalbigenin (**148**), 2″,3″,2‴,3‴-diepoxylupalbigenin (**149**), lupalbigenin 7-*O*-benzoate (**150**), lupalbigenin 7,4′-di-*O*-benzoate (**151**), 7-*O*-propargylluaplbigenin (**152**), 7,4′-*O*-dipropargyllupalbigenin (**153**) and 7-*O*-[1⁗-(carboxymethyl)-1⁗,*H*-3⁗,4⁗,5⁗-triazole]lupalbigenin (**155**)

conducted in the present study were anti-butyrylcholinesterase (BuChE) activity. The assay results are shown in Tables 40 and 41.

Compounds **7** and **8** exhibited anti-butyrylcholinesterase activity stronger than galantamine, the reference anti-cholinesterase drug, with IC_{50} 1.44 and 2.19 μM, respectively. Whereas compounds **1**, **9** and **44** showed low activity. The analogues **124**, **125**, **133**, **136** and **144** synthesized from compound **1** exhibited higher BuChE inhibitory activity than the parent compound with IC_{50} of 6.07, 16.04, 12.58, 2.53 and 10.31 μM, respectively, and compound **136** exhibited significant activity of 1.2-fold higher than galantamine. The analogue **138** which was synthesized from compound **8** exhibited the strongest anti-BuChE activity, with the IC_{50} value of 0.64 μM, which was over 5-fold more active than galantamine. The results suggested that these analogues may be used as anti-BuChE structure lead for anti-Alzheimer disease.

CHAPTER 4

CONCLUSION

Structural Identification of Isolated Isoflavones

Phytochemical investigation of the stems of *Drris scandens* led to the isolation of seven known isoflavones, derrisisoflavone A (**1**), 5,7,4′-trihydroxy-6,8-diprenylisoflavone (**7**), lupalbigenin (**8**), scandinone (**9**), scanderone (**28**), osajin (**44**) and scandenin (**51**). The known compounds were identified by comparison of spectroscopic and physical data with those of reported values.

Structural Modification

Structursl modification of the isolated natural isoflavones **1**, **8** and **44** gave 32 analogues including derrisisoflvone A 7-*O*-acetate (**124**), derrisisoflavone A 4′-*O*-acetate (**125**), derrisisoflavone A 7,4′-di-*O*-acetate (**126**), lupalbigenin 7-*O*-acetate (**127**), lupalbigenin 4′-*O*-acetate (**128**), lupalbigenin 7,4′-di-*O*-acetate (**129**), osajin 4′-*O*-acetate (**130**), derrisisoflavone A 7-*O*-methyl ether (**131**), derrisisoflavone A 4′-*O*-methyl ether (**132**), derrisisoflavone A 7,4′-di-*O*-methyl ether (**133**), lupalbigenin 7-*O*-methyl ether (**134**), lupalbigenin 7,4′-di-*O*-methyl ether (**135**), 4′-*O*-

methylosajin (**43**), tetrahydroderrisisoflavone A (**136**), hexahydroderrisisoflavone A (**137**), dihydrolupalbigenin (**138**), tetrahydrolupalbigenin (**139**), hexahydrolupalbigenin (**140**), tetrahydroosajin (**141**), hexahydroosajin (**142**), tetrahydrolupalbigenin 7-*O*-methyl ether (**143**), derrisisoflavone A 7-*O*-propanoate (**144**), derrisisoflavone A 4′-*O*-propanoate (**145**), derrisisoflavone A 7,4′-di-*O*-propanoate (**146**), 5′-nitrolupalbigenin (**147**), 2‴,3‴-epoxylupalbigenin (**148**), 2″,3″,2‴,3‴-diepoxylupalbigenin (**149**), lupalbigenin 7-*O*-benzoate (**150**), lupalbigenin 7,4′-di-*O*-benzoate (**151**), 7-*O*-propargyllupalbigenin (**152**), 7,4′-di-*O*-propargyllupalbigenin (**153**) and 7-*O*-[1⁗-(carboxymethyl)-1⁗,*H*-3⁗,4⁗,5⁗-triazole]lupalbigenin (**155**).

Biological Activities

The natural isoflavones, derrisisoflavone A (**1**), 5,7,4′-Trihydroxy-6,8-diprenylisoflavone (**7**), lupalbienin (**8**), scandinone (**9**), scanderone (**28**), osajin (**44**) and scandenin (**51**) and modified analogues, derrisisoflvone A 7-*O*-acetate (**124**), derrisisoflavone A 4′-*O*-acetate (**125**), derrisisoflavone A 7,4′-di-*O*-acetate (**126**), lupalbigenin 7-*O*-acetate (**127**), lupalbigenin 4′-*O*-acetate (**128**), lupalbigenin 7,4′-di-*O*-acetate (**129**), osajin 4′-*O*-acetate (**130**), derrisisoflavone A 7-*O*-methyl ether (**131**), derrisisoflavone A 4′-*O*-methyl ether (**132**), derrisisoflavone A 7,4′-di-*O*-methyl ether (**133**), lupalbigenin 7-*O*-methyl ether (**134**), lupalbigenin 7,4′-di-*O*-methyl ether (**135**), 4′-*O*-

methylosajin (**43**), tetrahydroderrisisoflavone A (**136**), hexahydroderrisisoflavone A (**137**), dihydrolupalbigenin (**138**), tetrahydrolupalbigenin (**139**), hexahydrolupalbigenin (**140**), tetrahydroosajin (**141**), hexahydroosajin (**142**), tetrahydrolupalbigenin 7-*O*-methyl ether (**143**), derrisisoflavone A 7-*O*-propanoate (**144**), derrisisoflavone A 4′-*O*-propanoate (**145**), derrisisoflavone A 7,4′-di-*O*-propanoate (**146**), 5′-nitrolupalbigenin (**147**), 2‴,3‴-epoxylupalbigenin (**148**), 2″,3″,2‴,3‴-diepoxylupalbigenin (**149**), lupalbigenin 7-*O*-benzoate (**150**), lupalbigenin 7,4′-di-*O*-benzoate (**151**), 7-*O*-propargyllupalbigenin (**152**), 7,4′-di-*O*-propargyllupalbigenin (**153**) and 7-*O*-[1⁗-(carboxymethyl)-1⁗,*H*-3⁗,4⁗,5⁗-triazole]lupalbigenin (**155**) were tested for anti-butyrylcholinesterase (BuChE) activity. Compound **138** exhibited strongest anti-butyrylcholinesterase followed by compounds **138**, **7**, **8**, **136**, **140**, **124**, **139**, **150**, **147** and **144** which showed the IC_{50} values of 0.64, 1.44, 2.19, 2.53, 4.73, 6.07, 6.64, 7.48, 7.83 and 10.31 μM, respectively.

APPENDICES

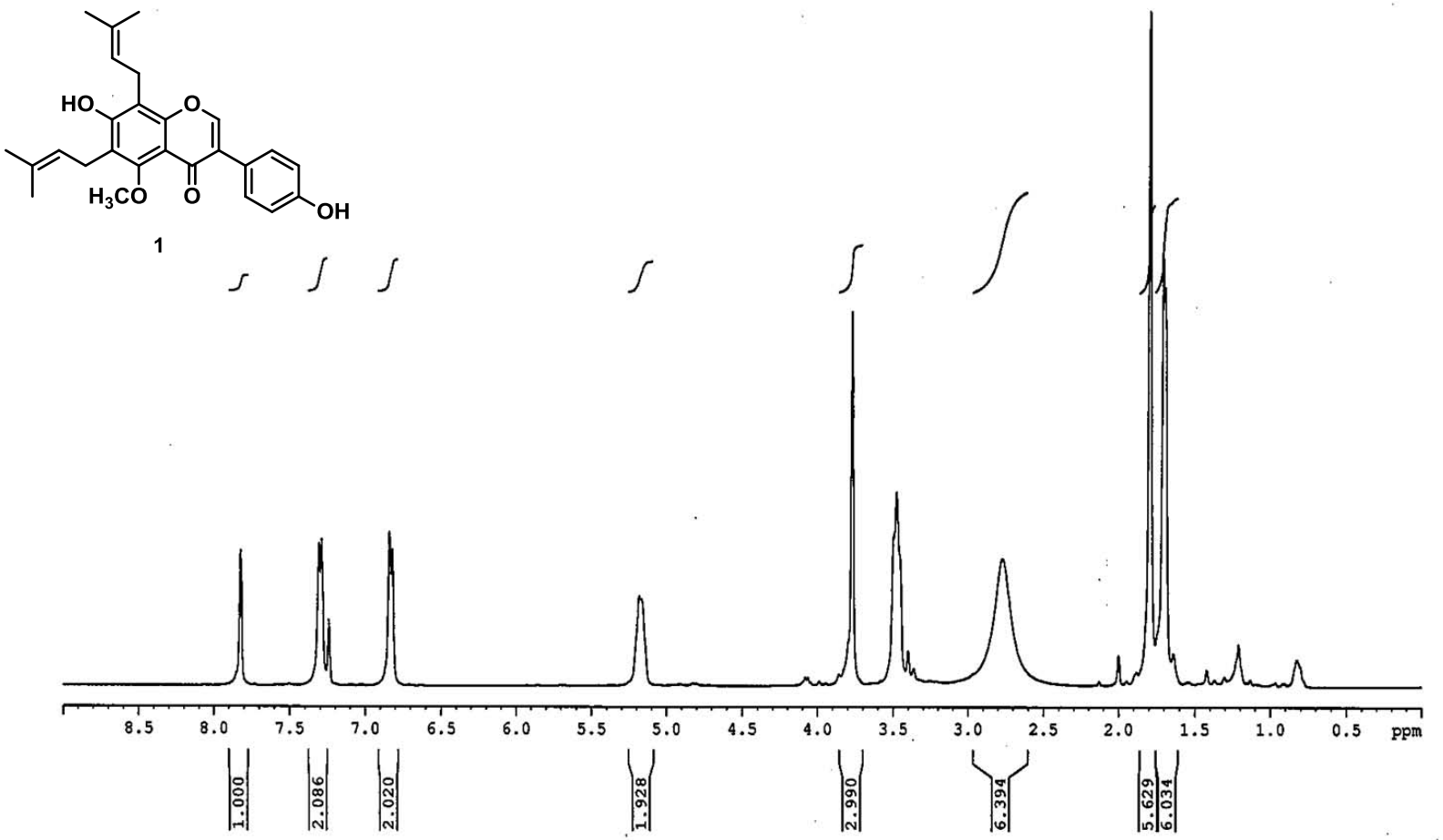


Figure 1 ^{1}H-NMR Spectrum of Derrisisoflavone A (**1**) in $CDCl_3$

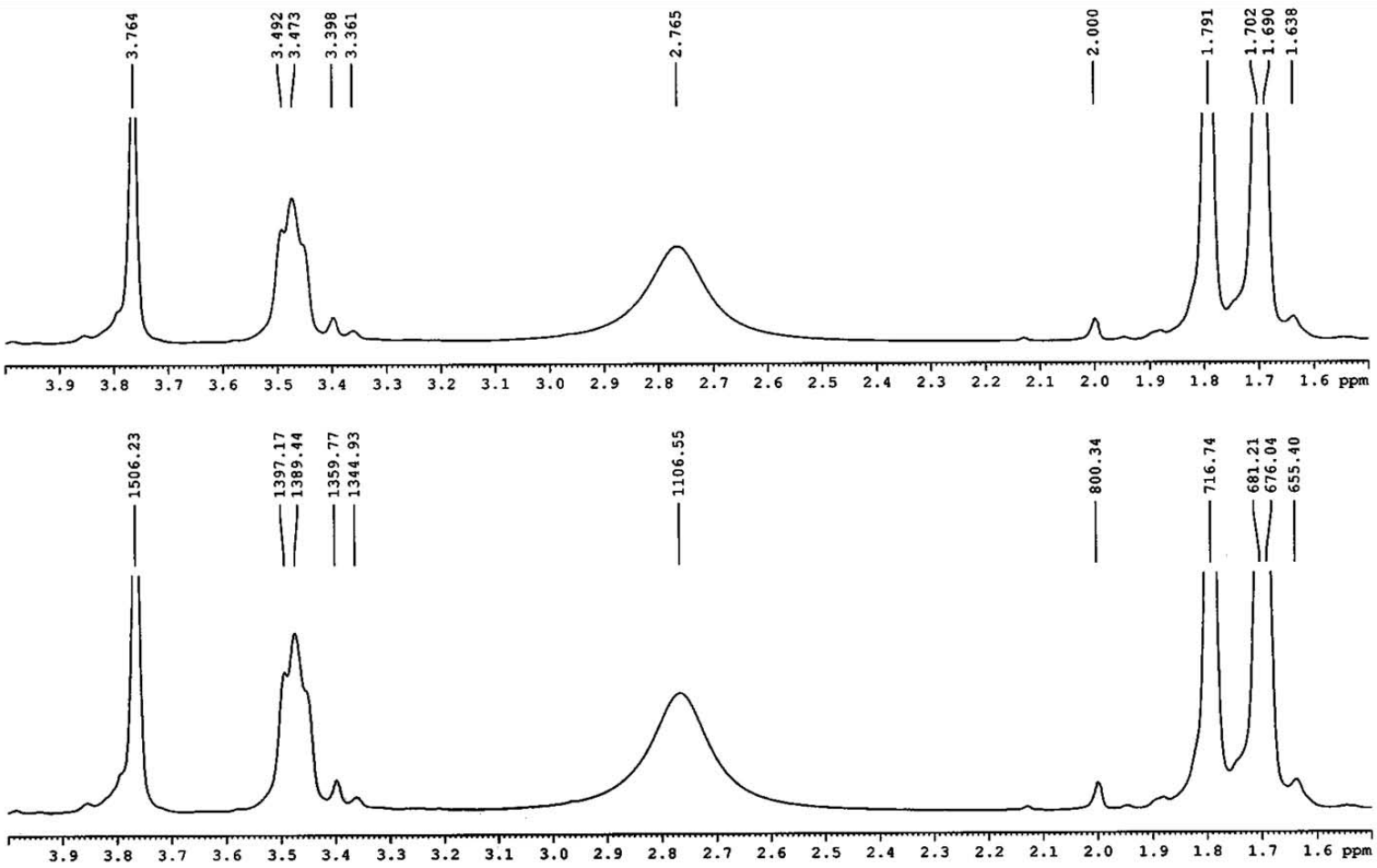


Figure 1a Expansion of ^{1}H-NMR Spectrum of Derrisisoflavone A (**1**) in $CDCl_3$

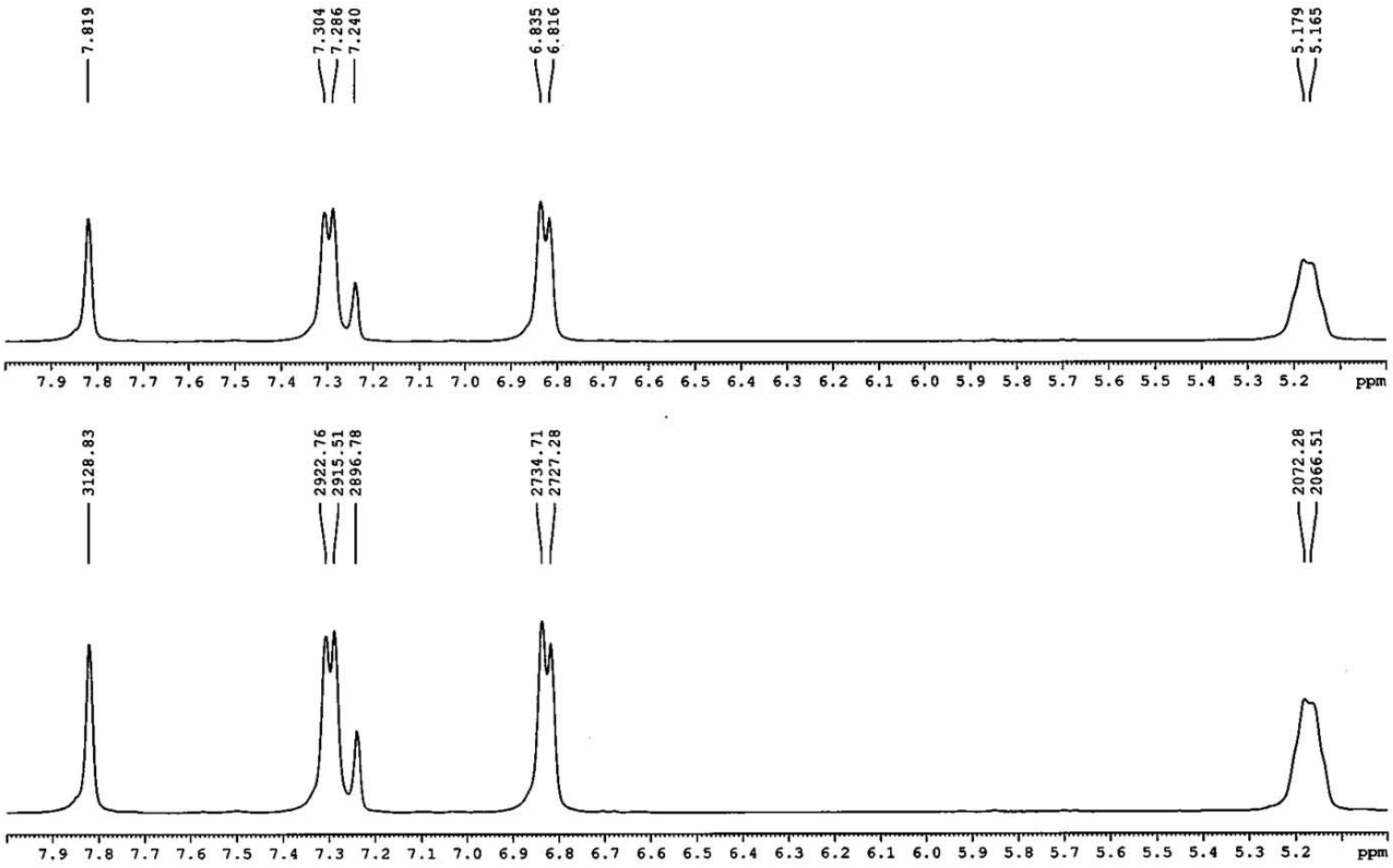


Figure 1b Expansion of ^{1}H-NMR Spectrum of Derrisisoflavone A (**1**) in $CDCl_3$

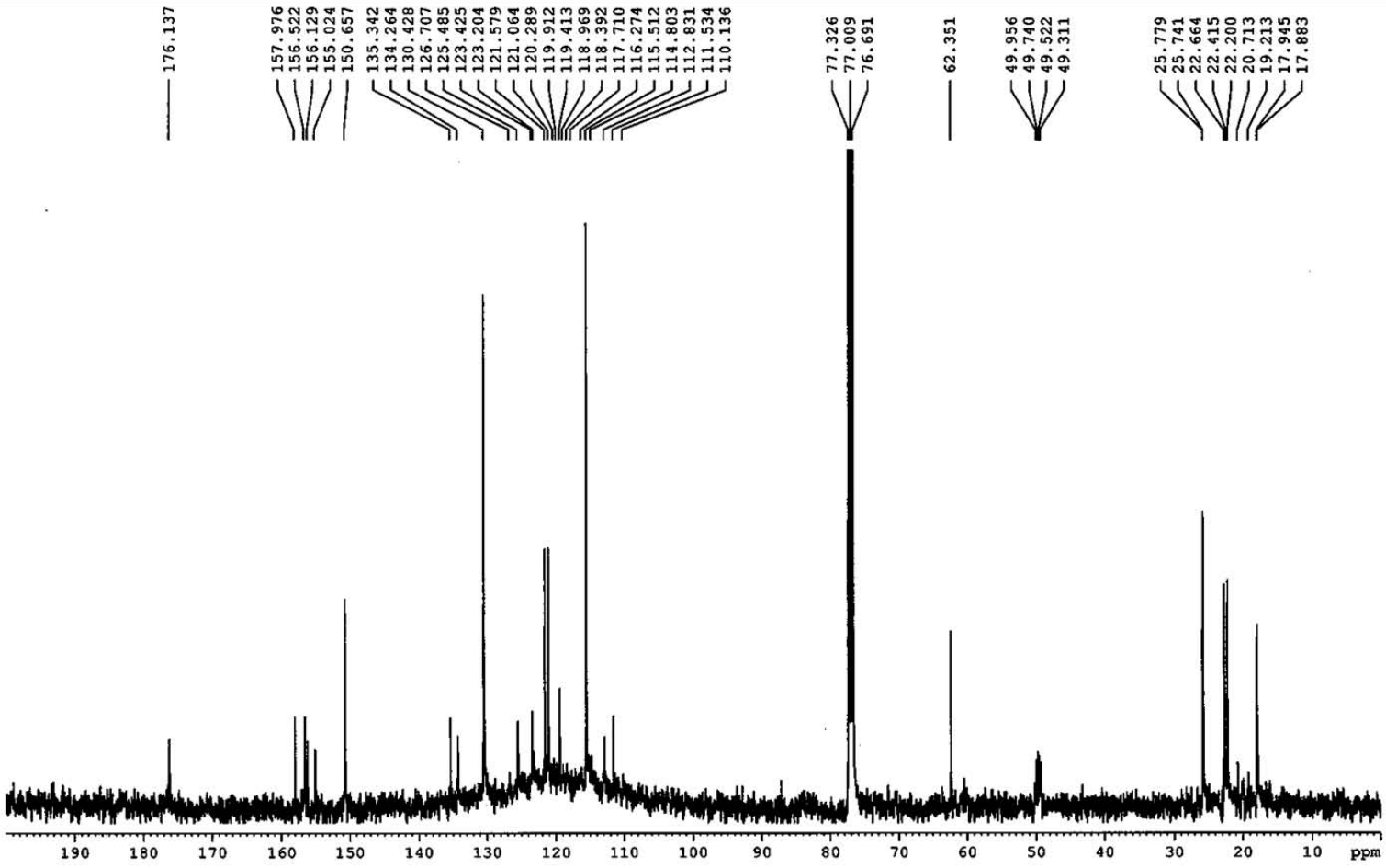


Figure 1c ^{13}C-NMR Spectrum of Derrisisoflavone A (**1**) in $CDCl_3$

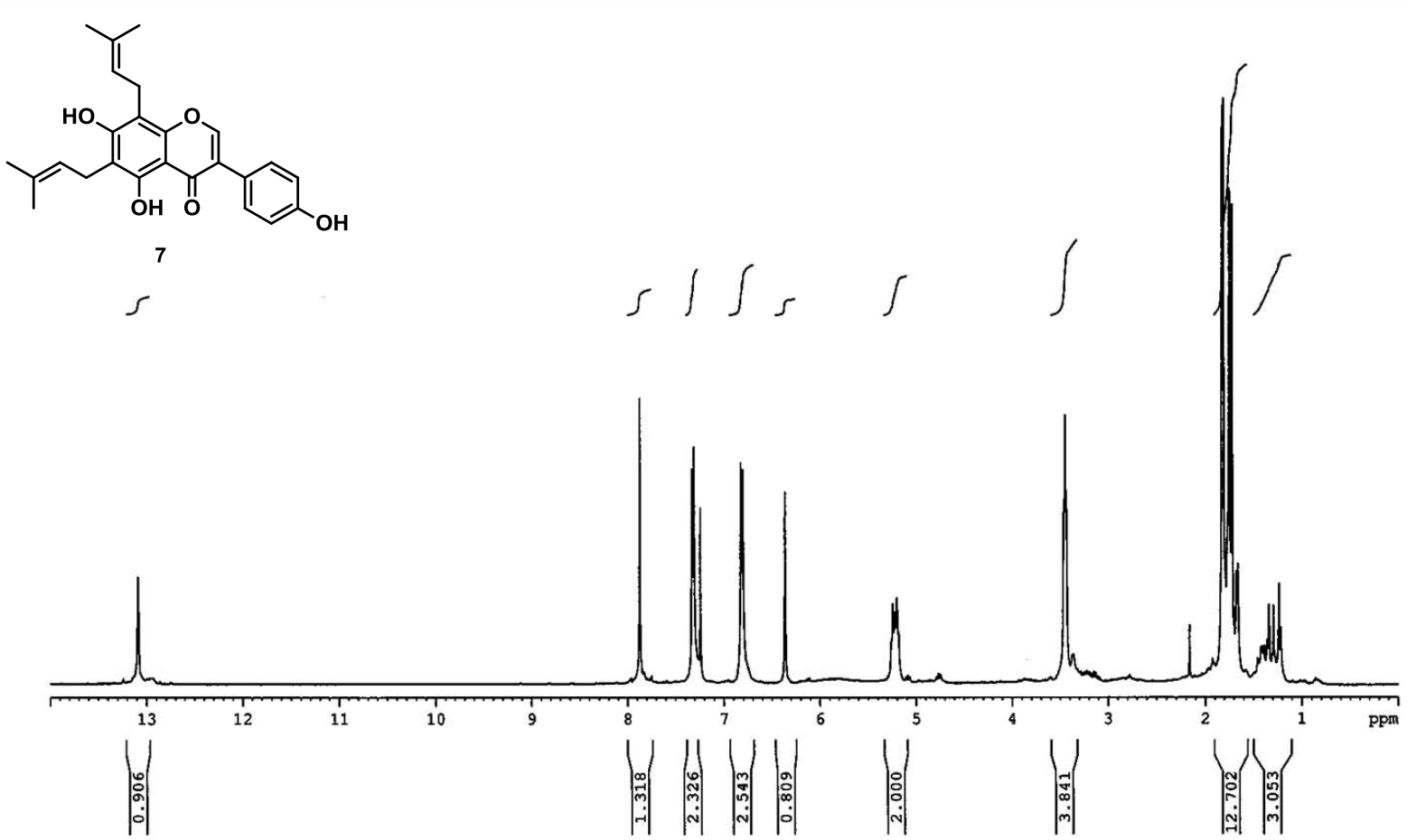


Figure 2 ^{1}H-NMR Spectrum of 5,7,4′-Trihydroxy-6,8-diphenylisoflavone (**7**) in $CDCl_3$

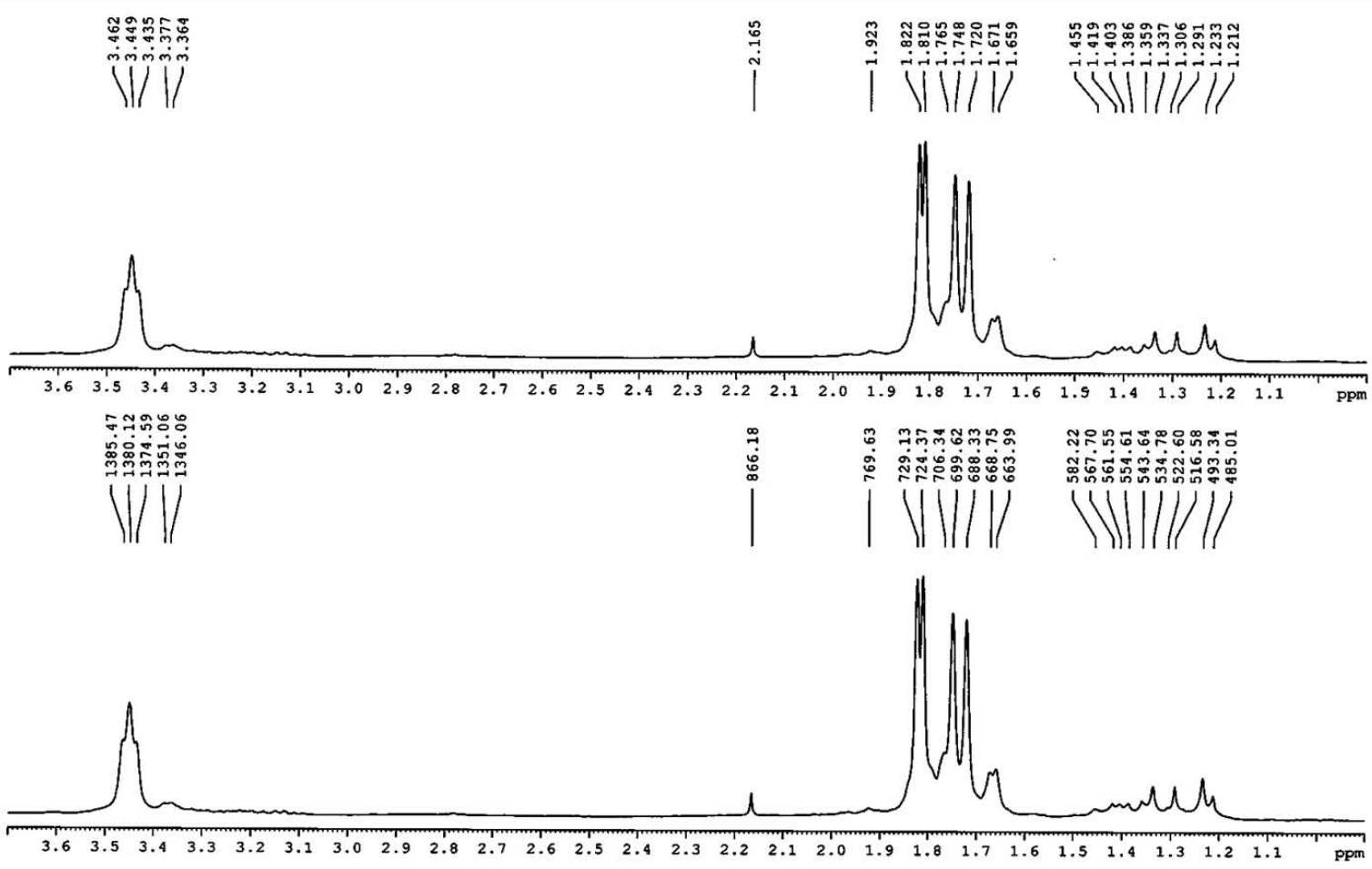


Figure 2a Expansion of ^{1}H-NMR Spectrum of 5,7,4′-Trihydroxy-6,8-diphenylisoflavone (**7**) in $CDCl_3$

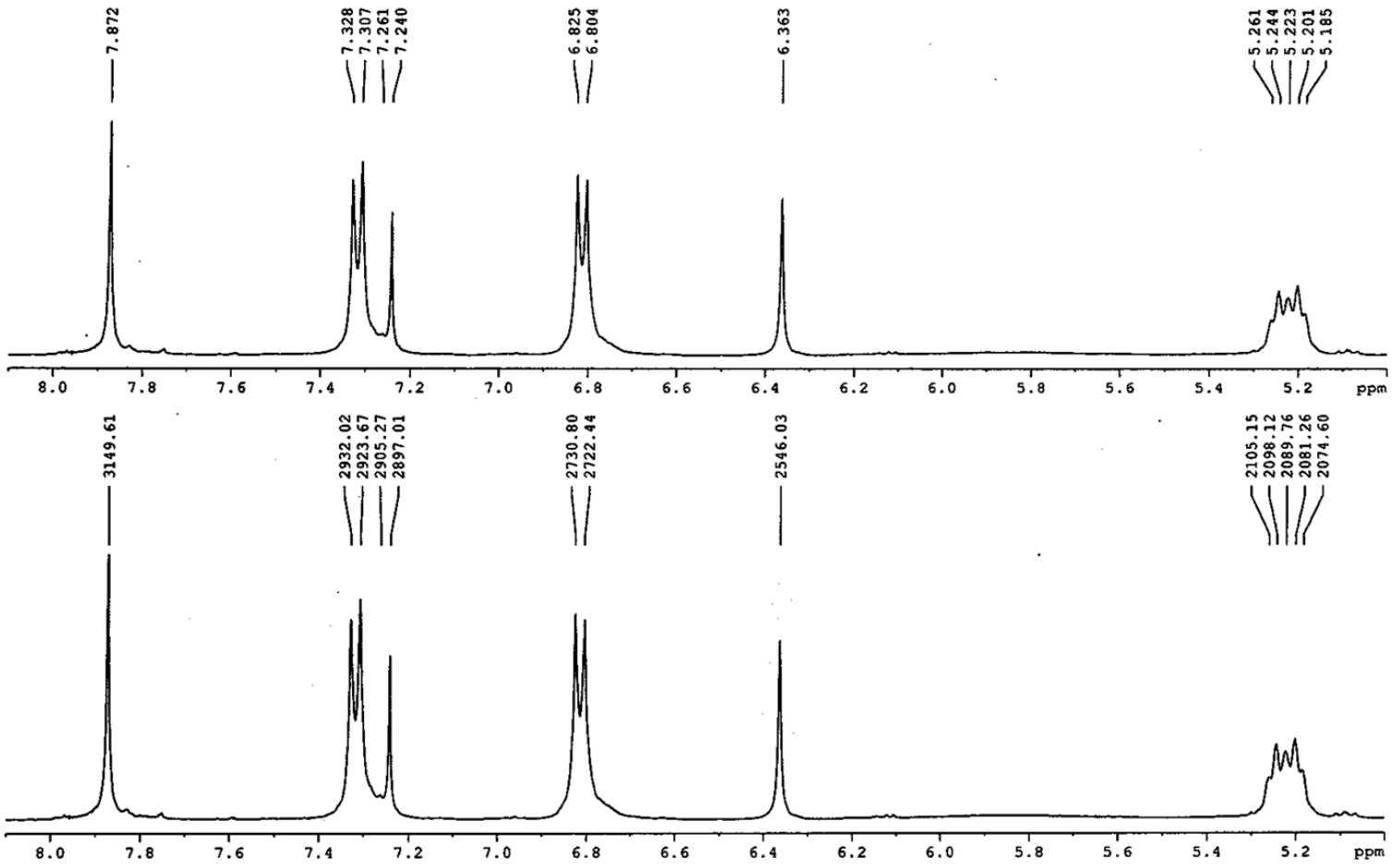


Figure 2b Expansion of ^{1}H-NMR Spectrum of 5,7,4′-Trihydroxy-6,8-diphenylisoflavone (**7**) in $CDCl_3$

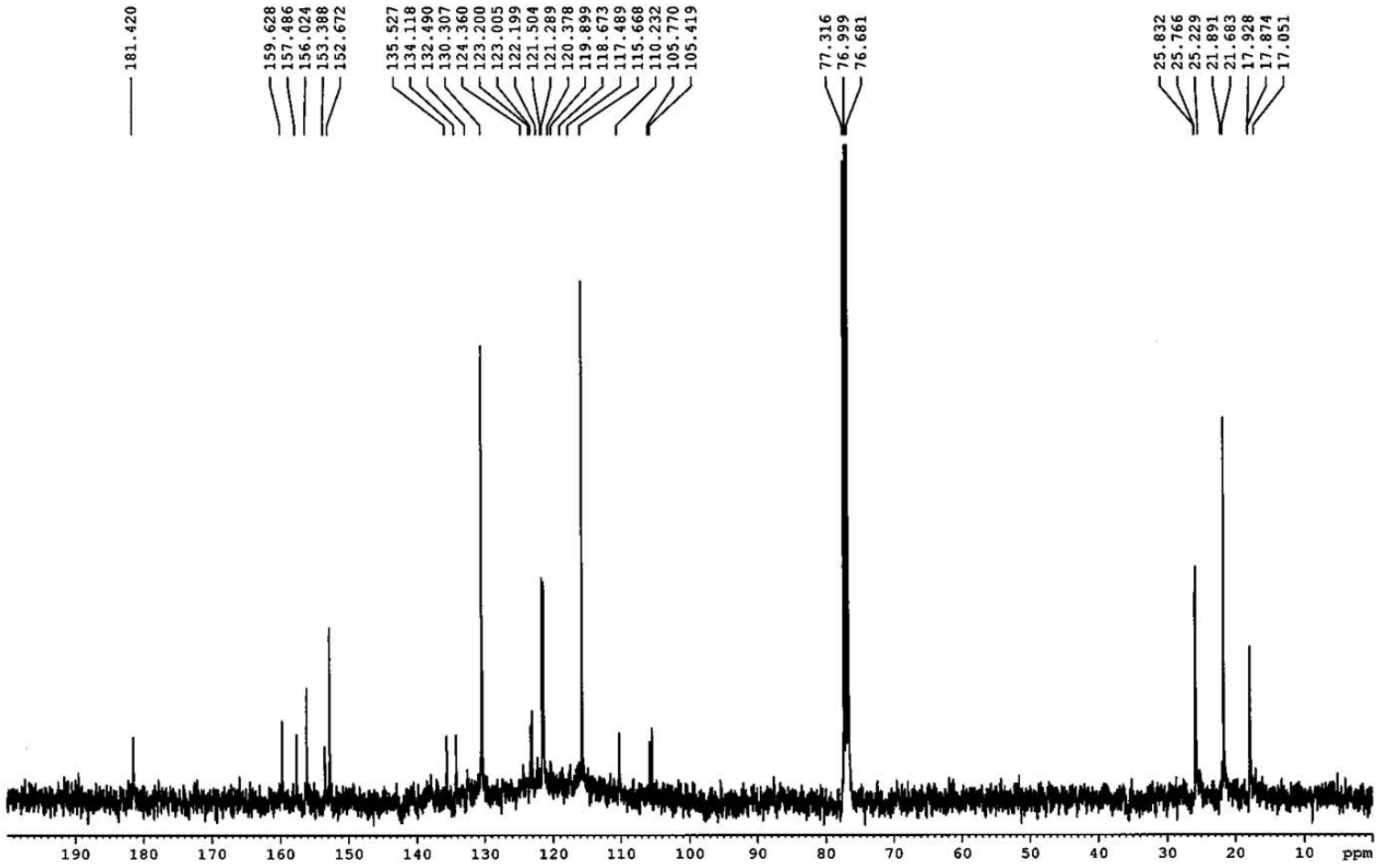


Figure 2c ^{13}C-NMR Spectrum of 5,7,4′-Trihydroxy-6,8-diphenylisoflavone (**7**) in $CDCl_3$

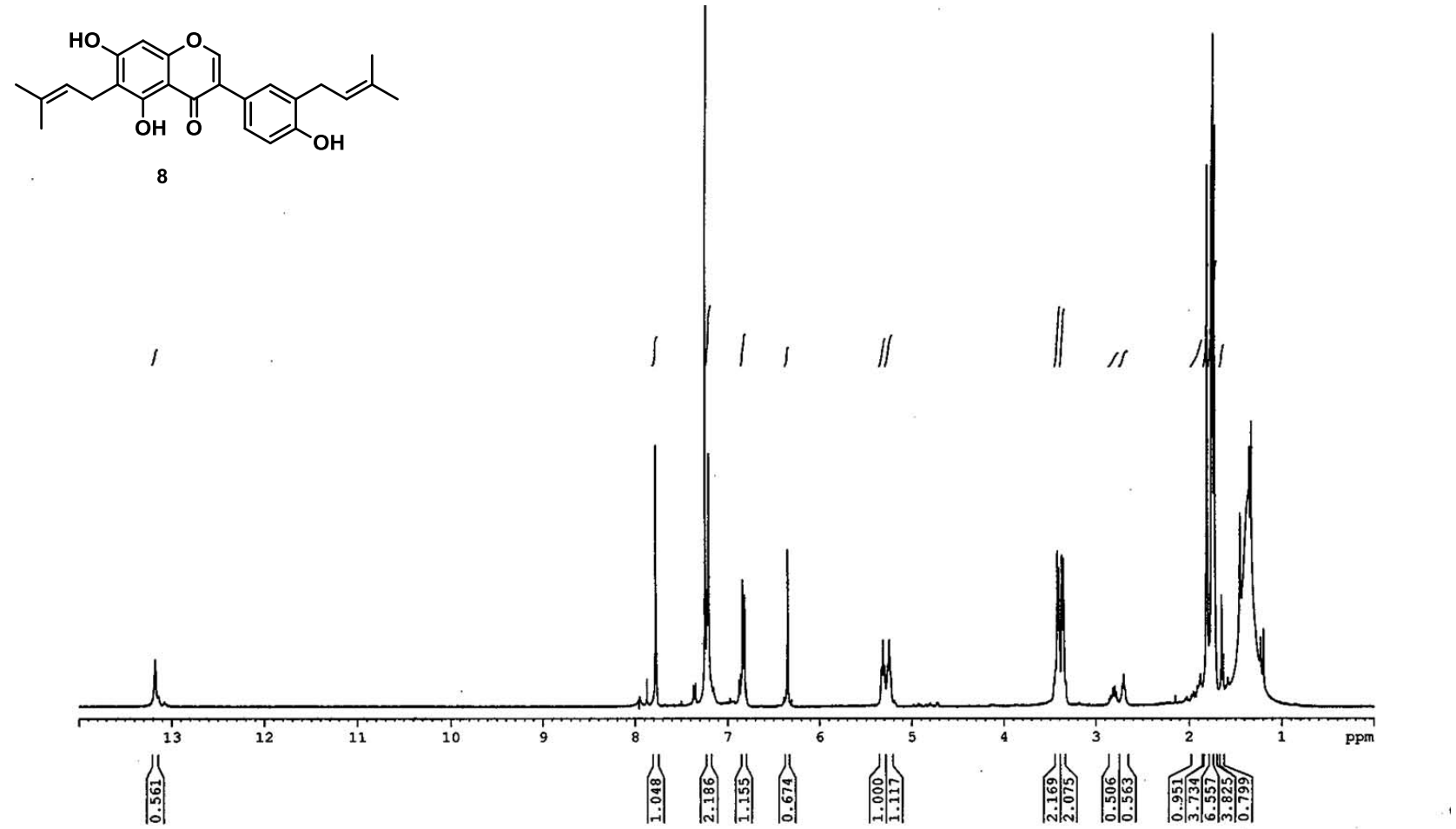


Figure 3 ^{1}H-NMR Spectrum of Lupalbigenin (**8**) in $CDCl_3$

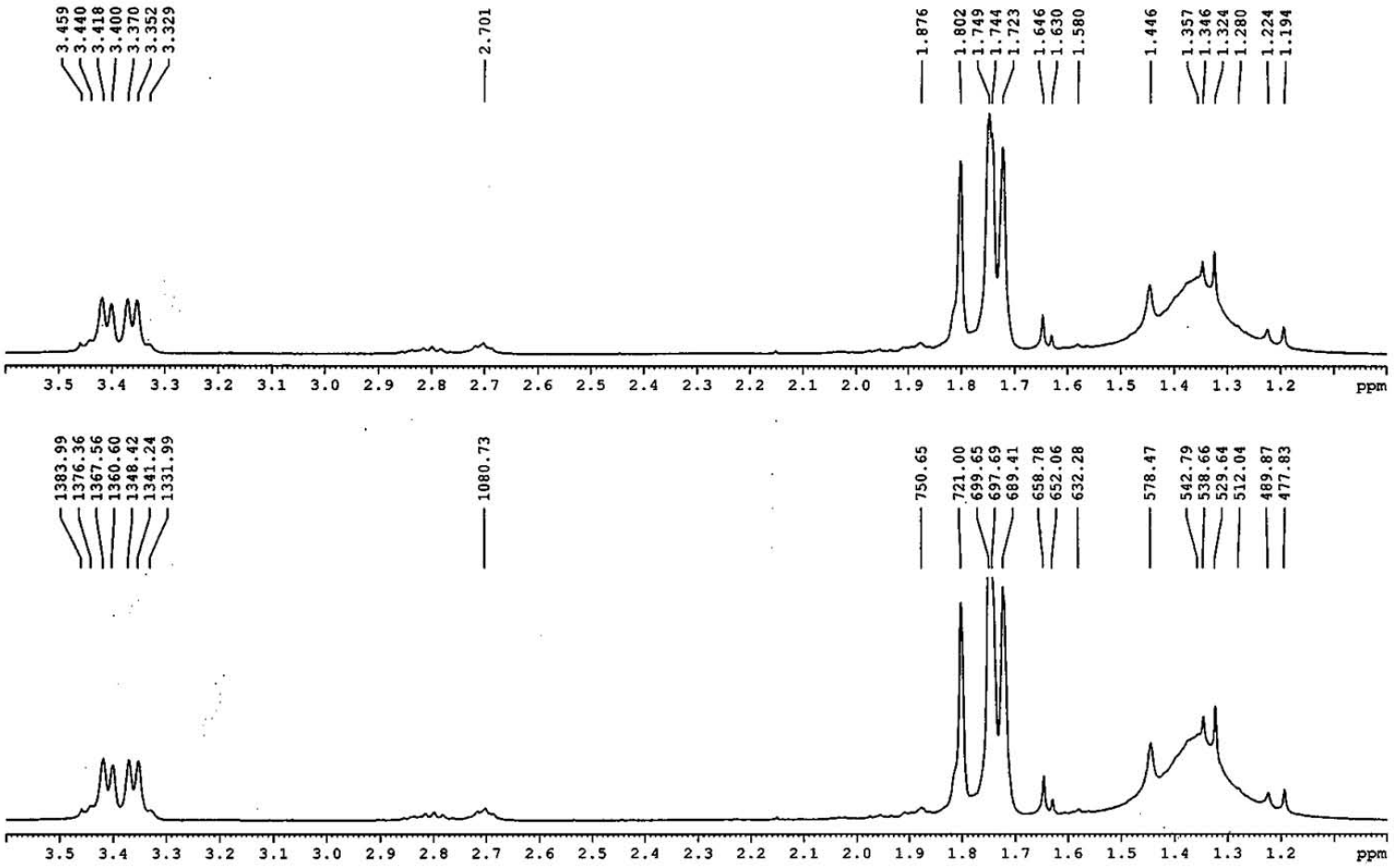


Figure 3a Expansion of ^{1}H-NMR Spectrum of Lupalbigenin (**8**) in $CDCl_3$

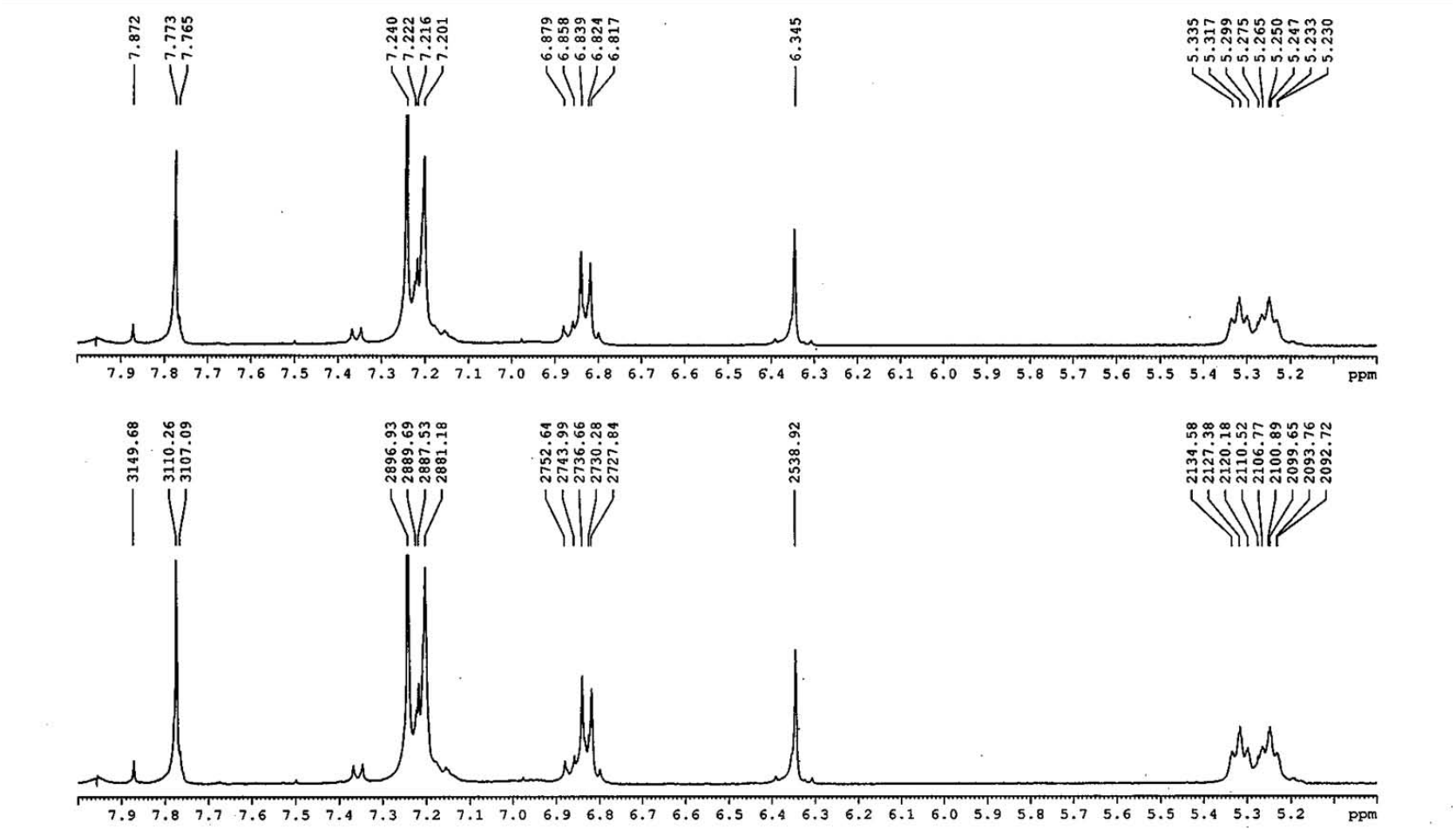


Figure 3b Expansion of ^{1}H-NMR Spectrum of Lupalbigenin (**8**) in $CDCl_3$

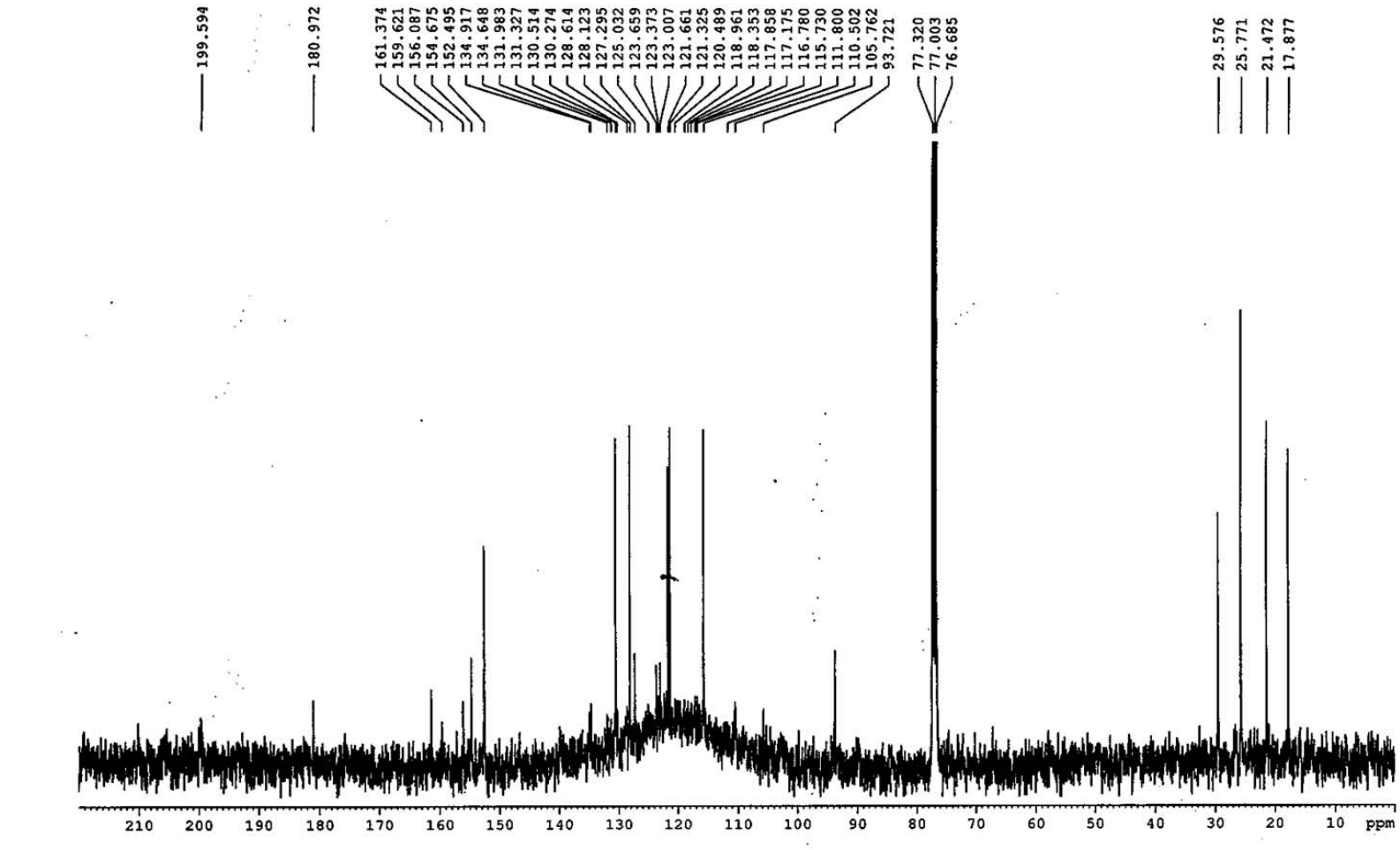


Figure 3c ^{13}C-NMR Spectrum of Lupalbigenin (**8**) in $CDCl_3$

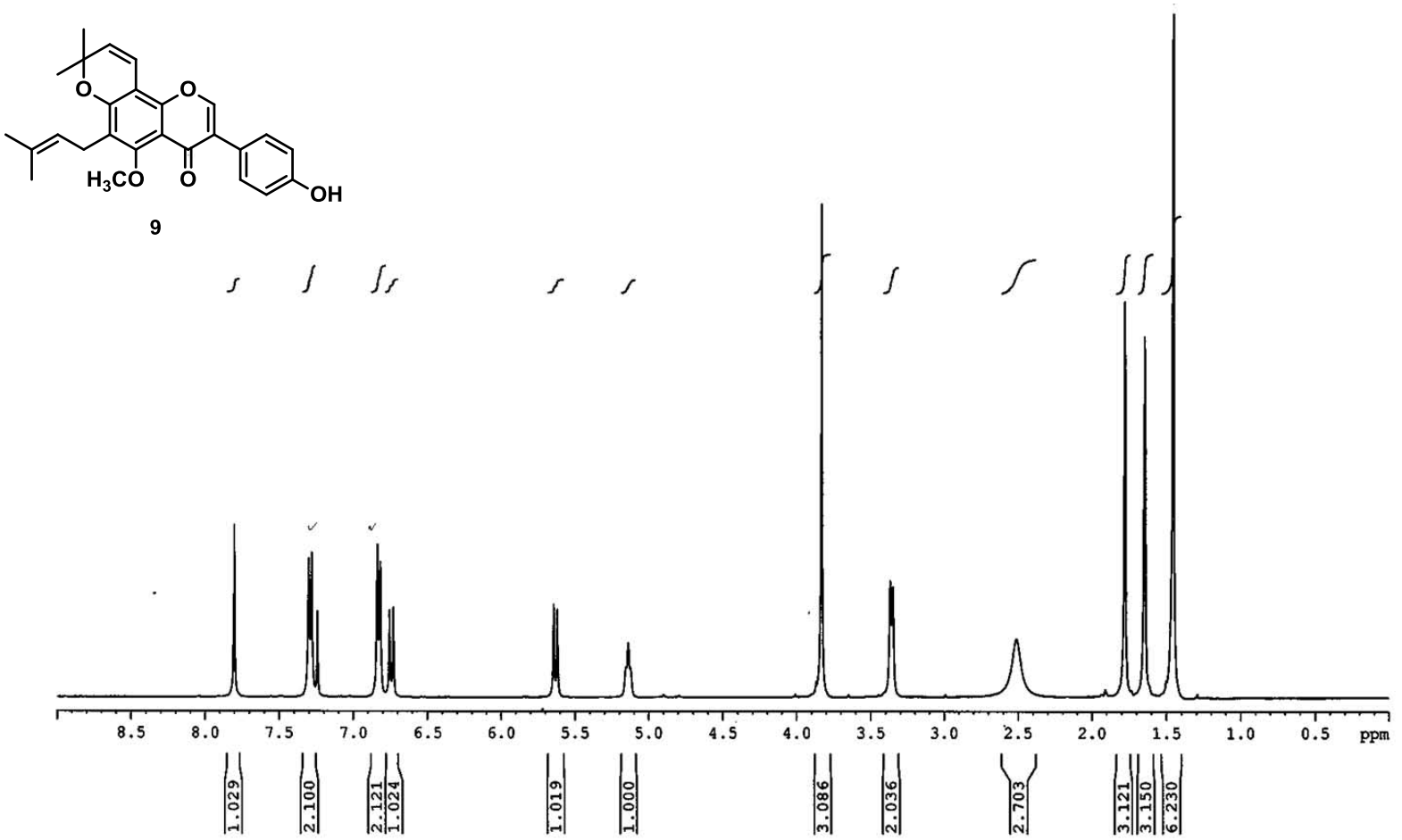


Figure 4 ^{1}H-NMR Spectrum of Scandinone (**9**) in $CDCl_3$ + 2 Drops of CD_3OD

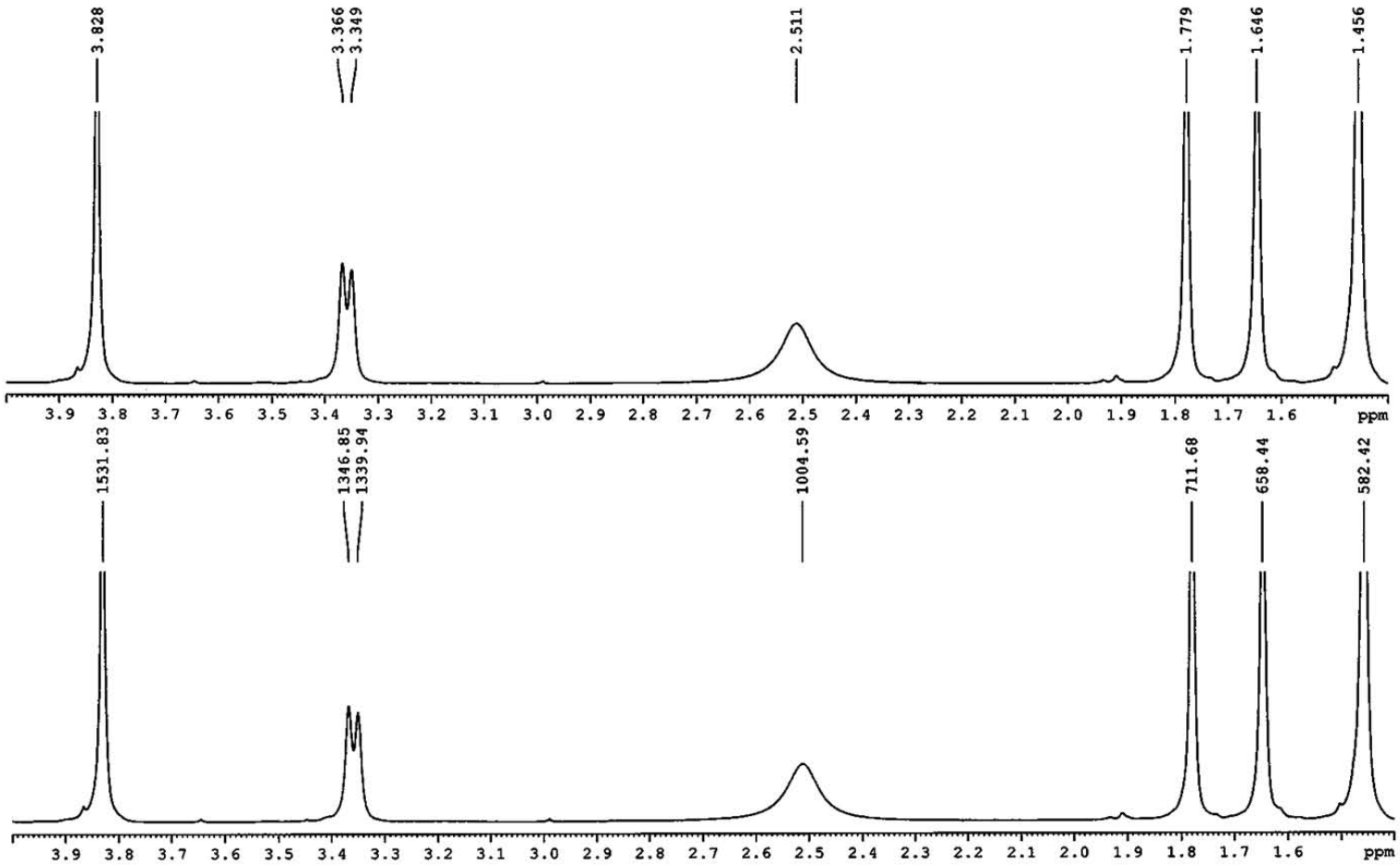


Figure 4a Expansion of ^{1}H-NMR Spectrum of Scandinone (**9**) in $CDCl_3$ + 2 Drops of CD_3OD

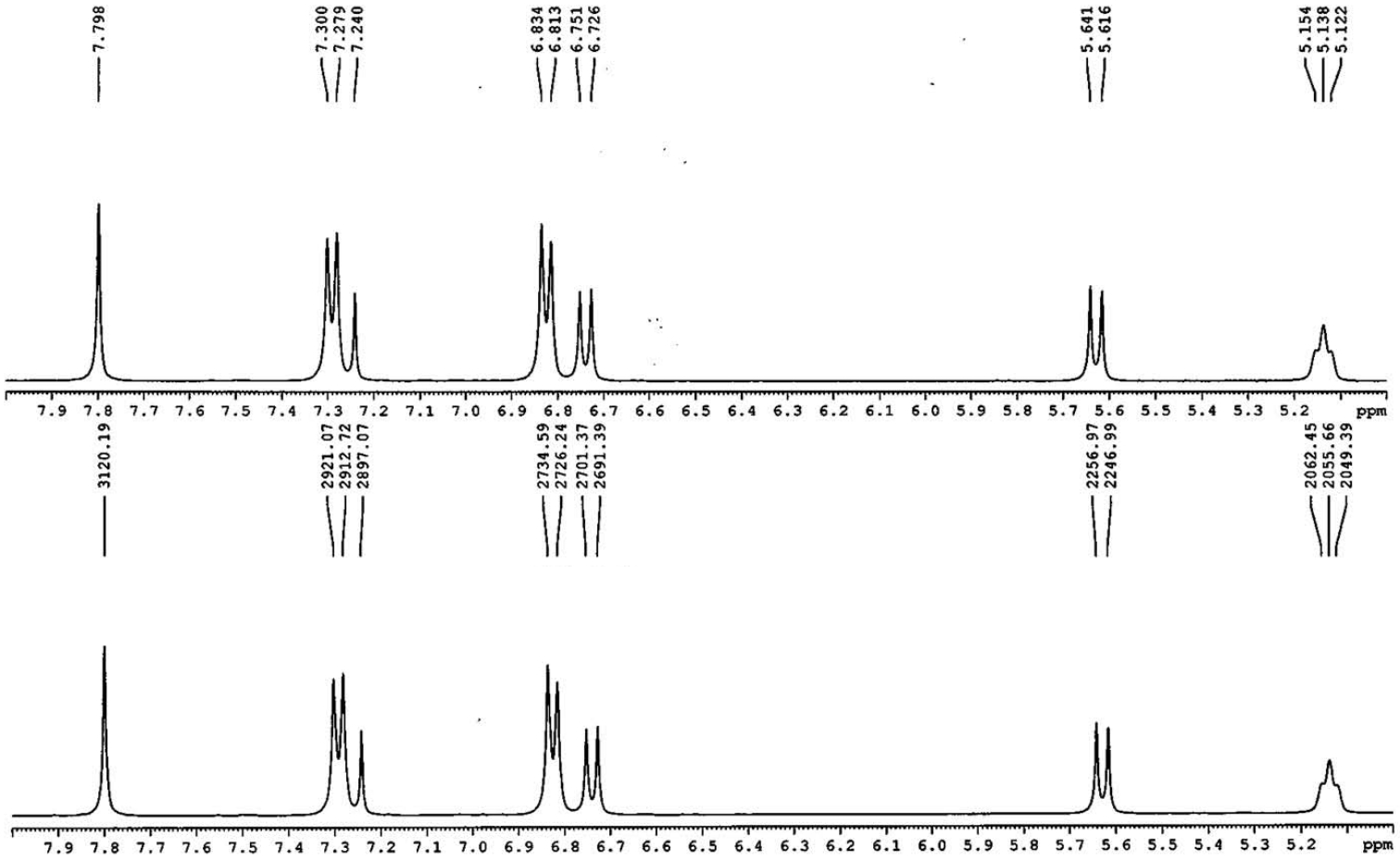


Figure 4b Expansion of ^{1}H-NMR Spectrum of Scandinone (**9**) in $CDCl_3$ + 2 Drops of CD_3OD

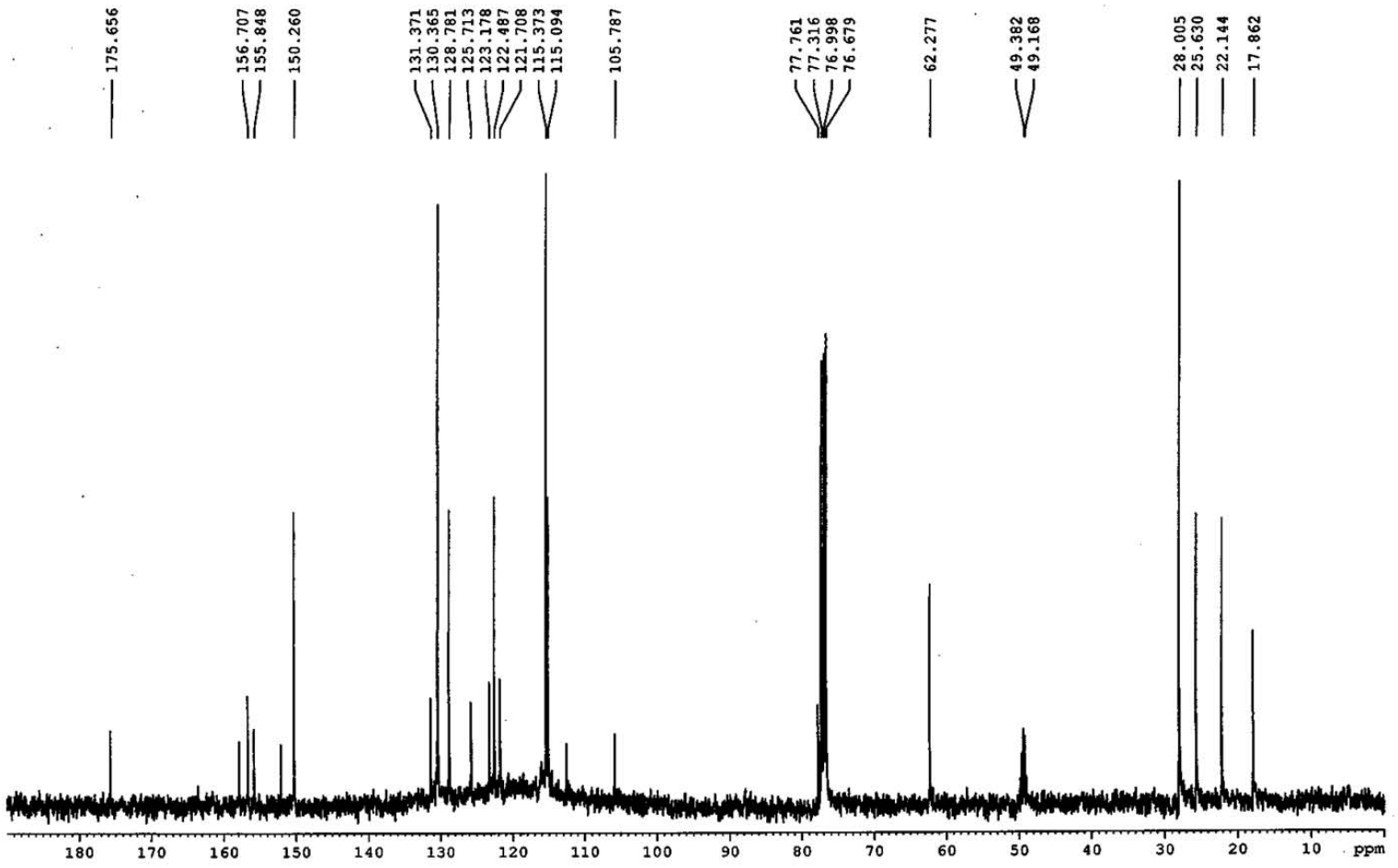


Figure 4c ^{13}C-NMR Spectrum of Scandinone (**9**) in $CDCl_3$ + 2 Drops of CD_3OD

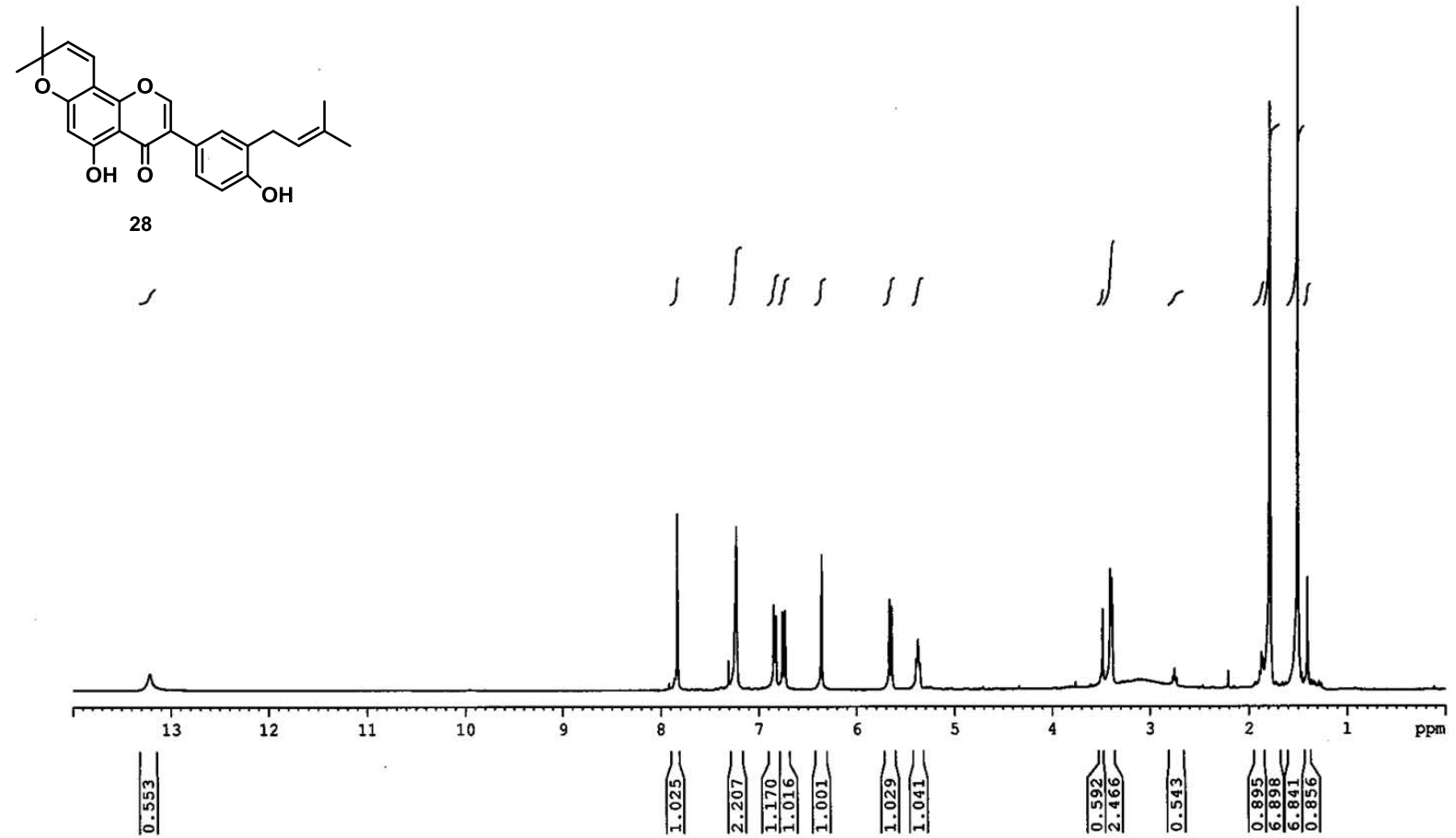


Figure 5 ^{1}H-NMR Spectrum of Scanderone (**28**) in $CDCl_3$ + 2 Drops of CD_3OD

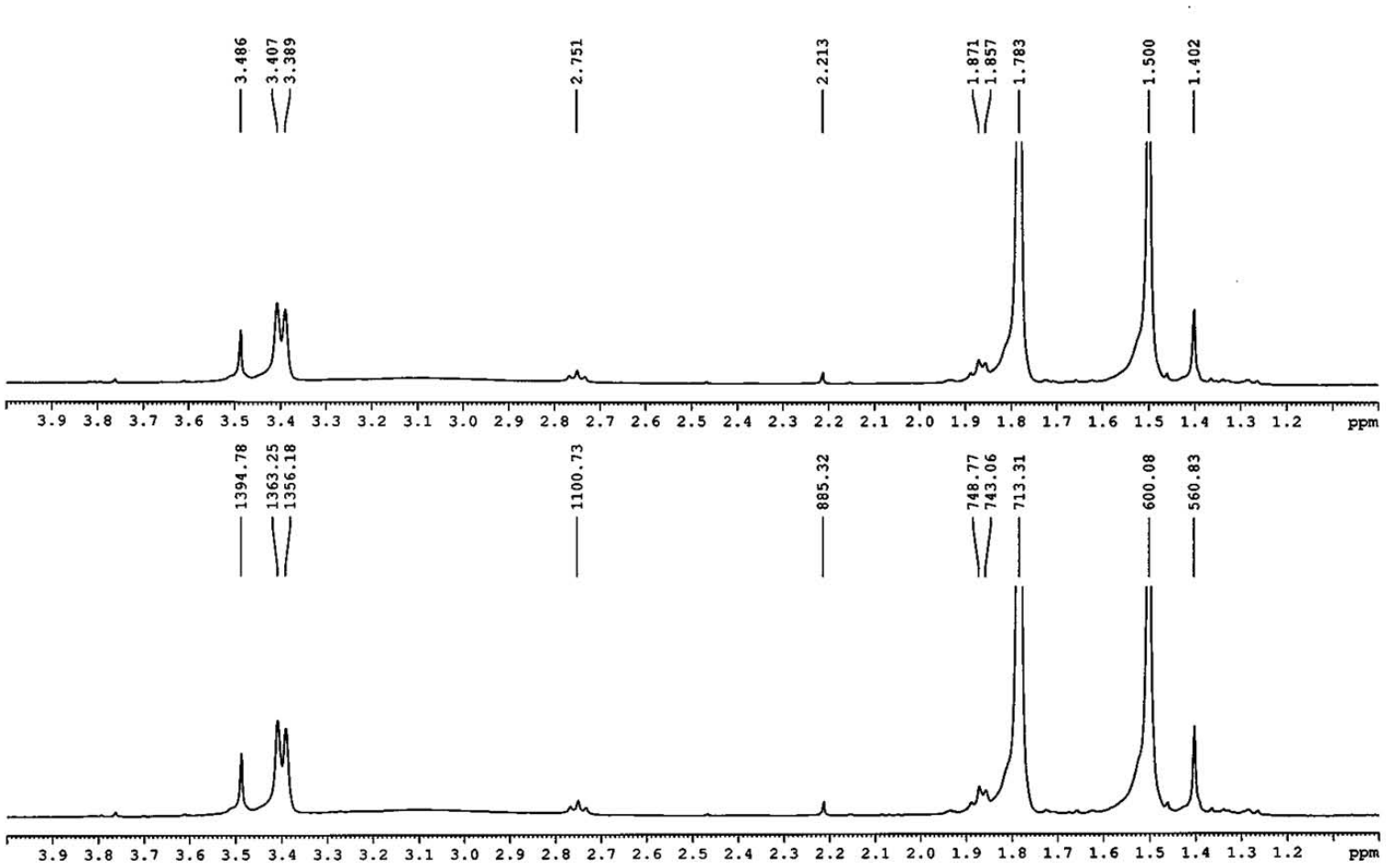


Figure 5a Expansion of ^{1}H-NMR Spectrum of Scanderone (**28**) in $CDCl_3$ + 2 Drops of CD_3OD

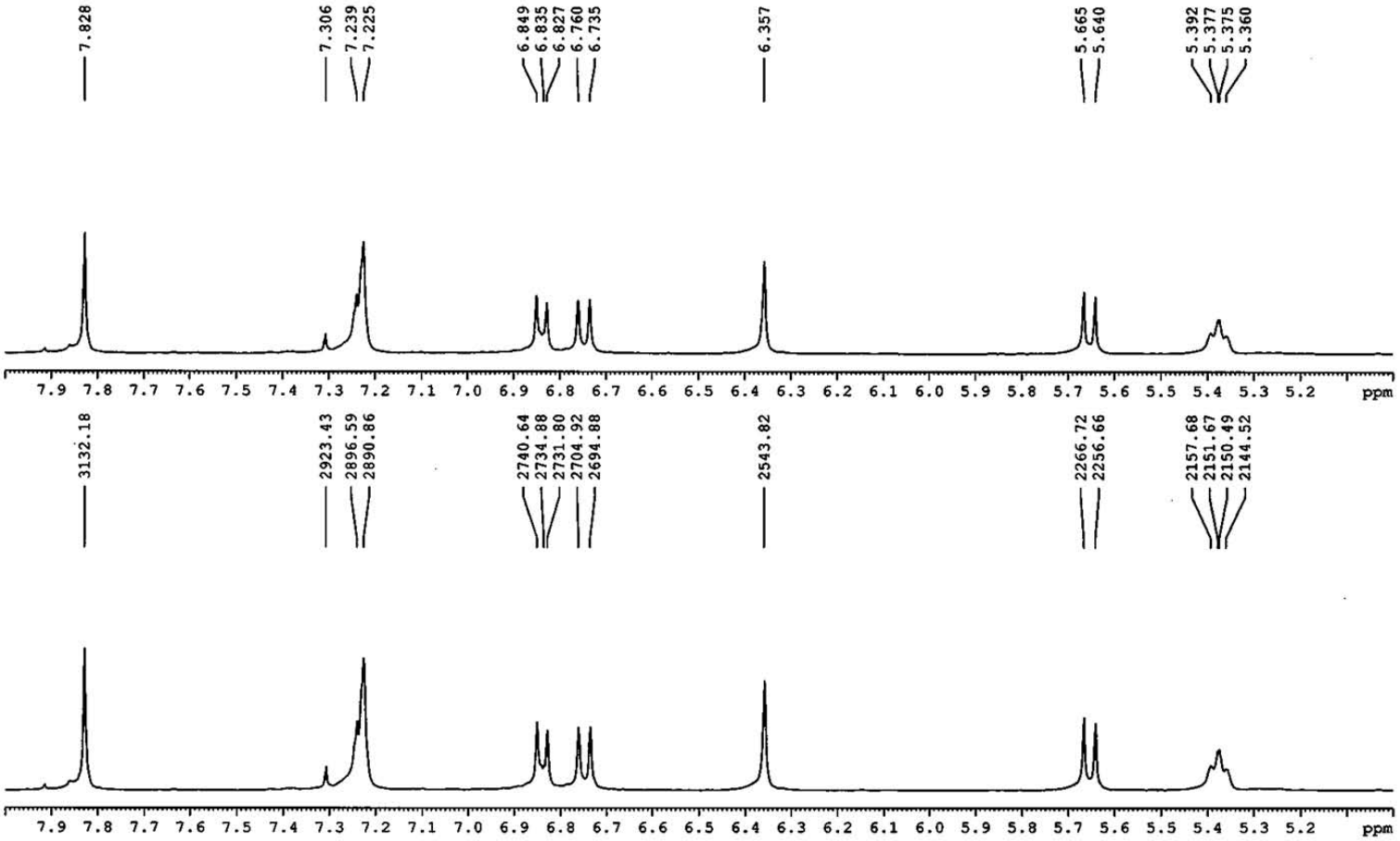


Figure 5b Expansion of ^{1}H-NMR Spectrum of Scanderone (**28**) in $CDCl_3$ + 2 Drops of CD_3OD

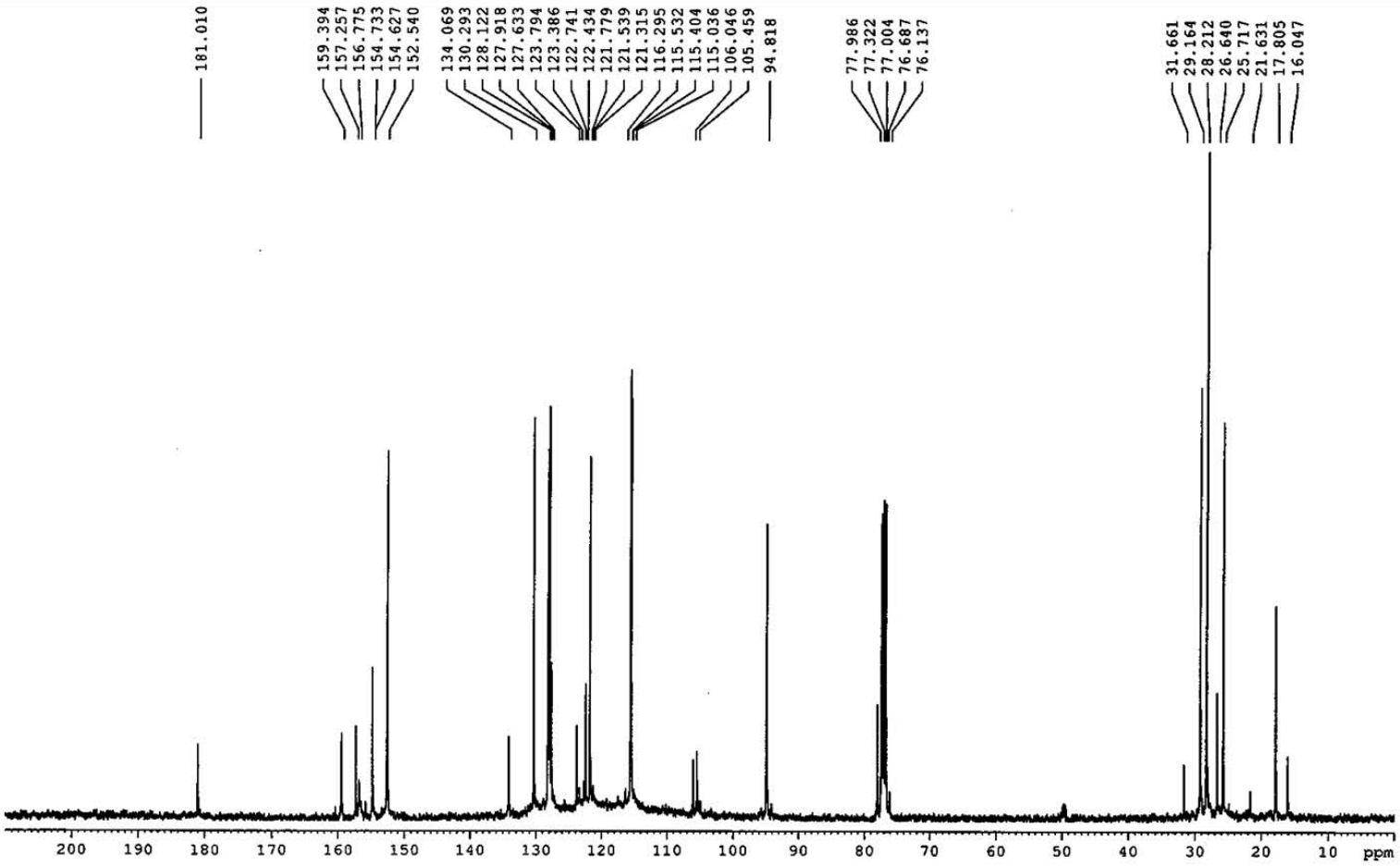


Figure 5c ^{13}C-NMR Spectrum of Scanderone (**28**) in $CDCl_3$ + 2 Drops of CD_3OD

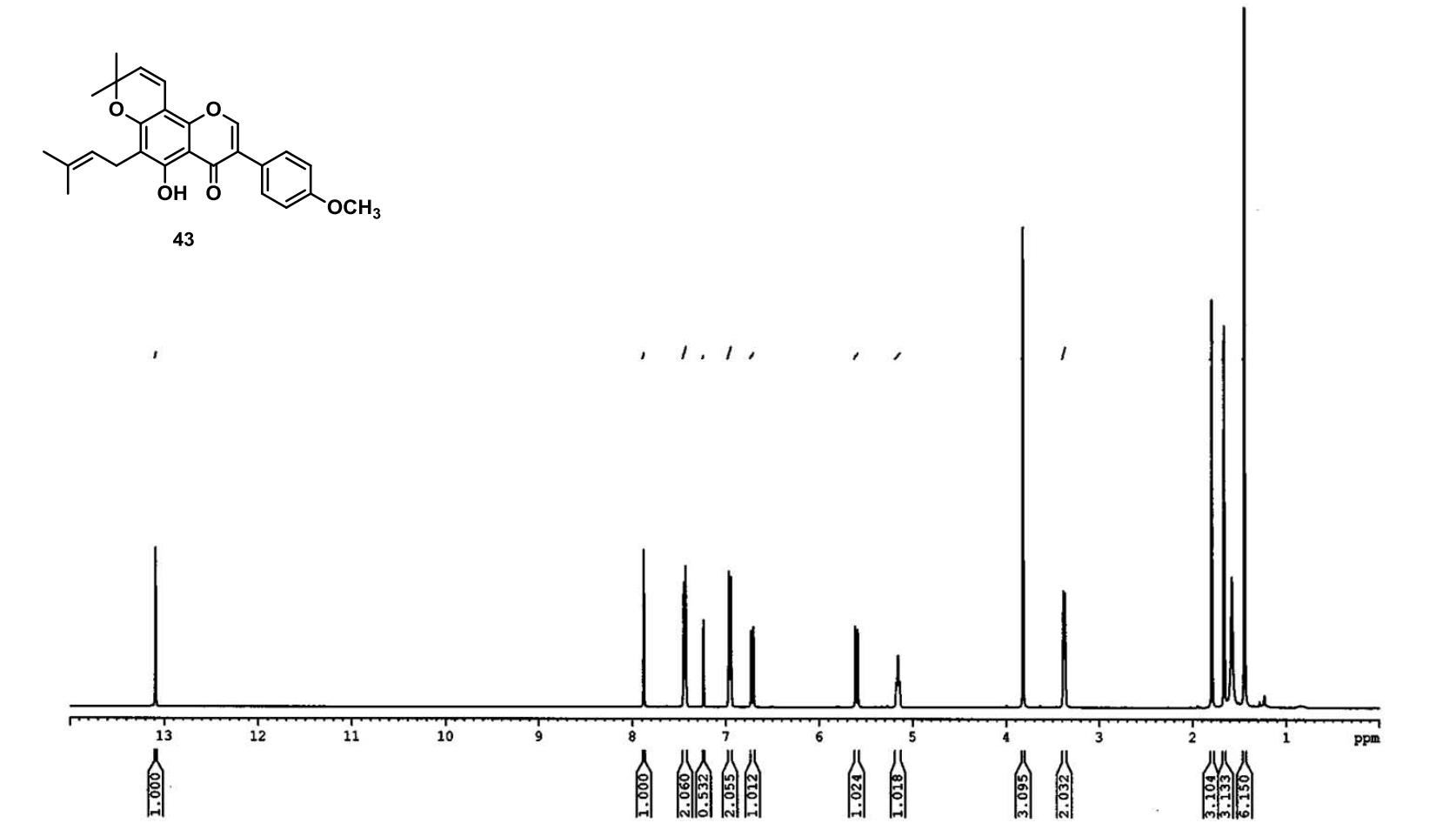


Figure 6 ^{1}H-NMR Spectrum of 4′-*O*-Methylosajin (**43**) in $CDCl_3$

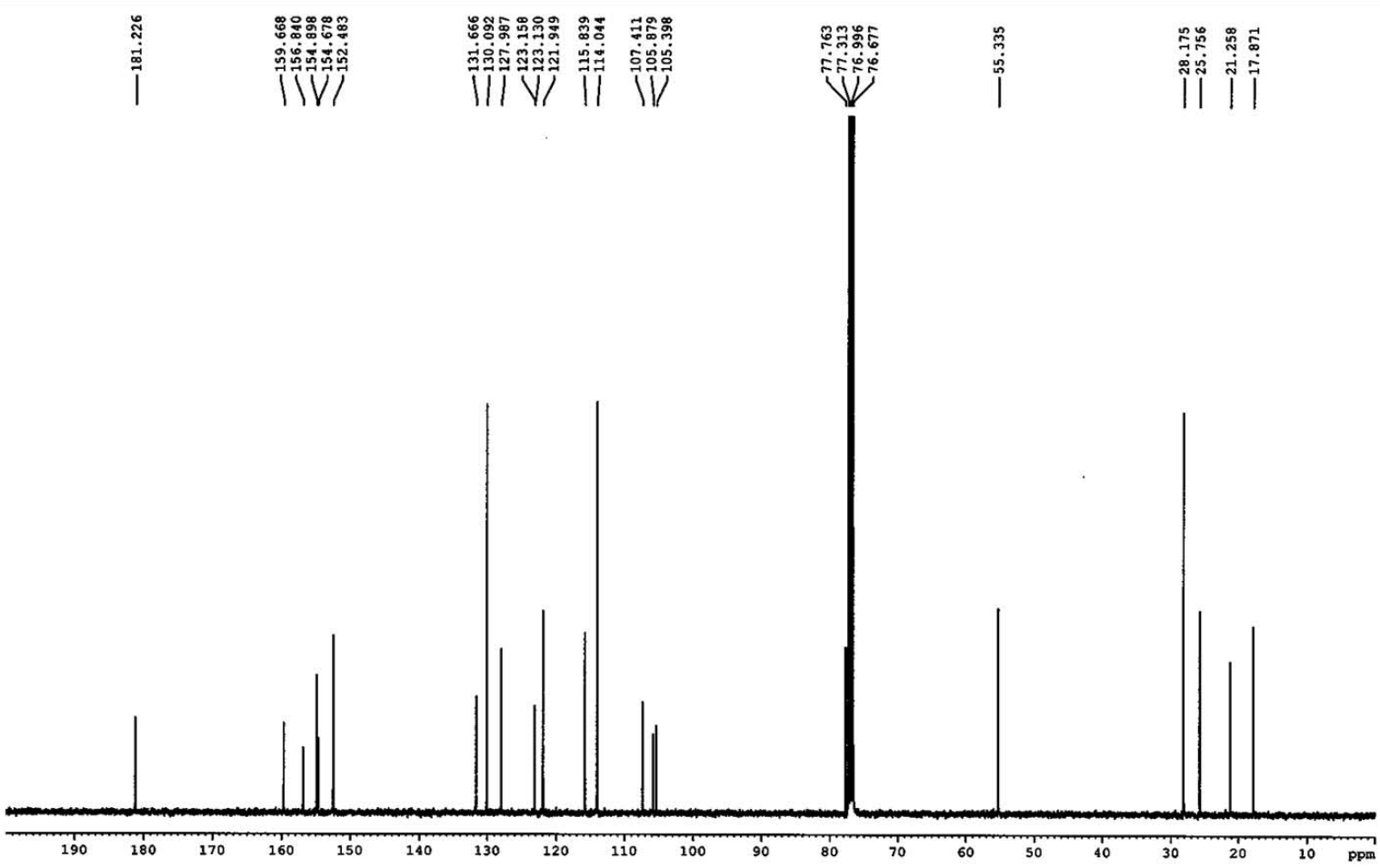


Figure 6a ^{13}C-NMR Spectrum of 4′-*O*-Methylosajin (**43**) in $CDCl_3$

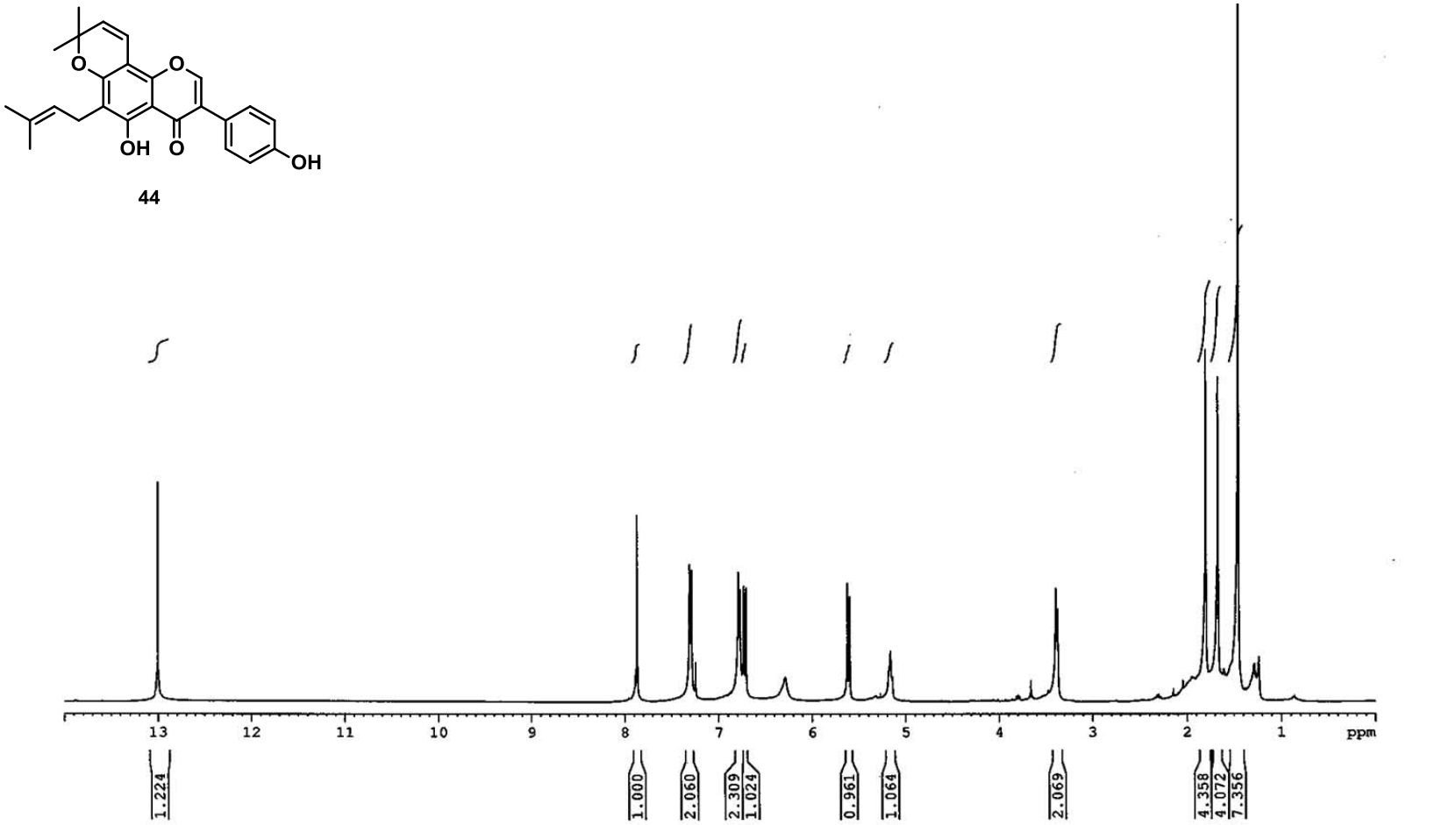


Figure 7 ^{1}H-NMR Spectrum of Osajin (**44**) in $CDCl_3$

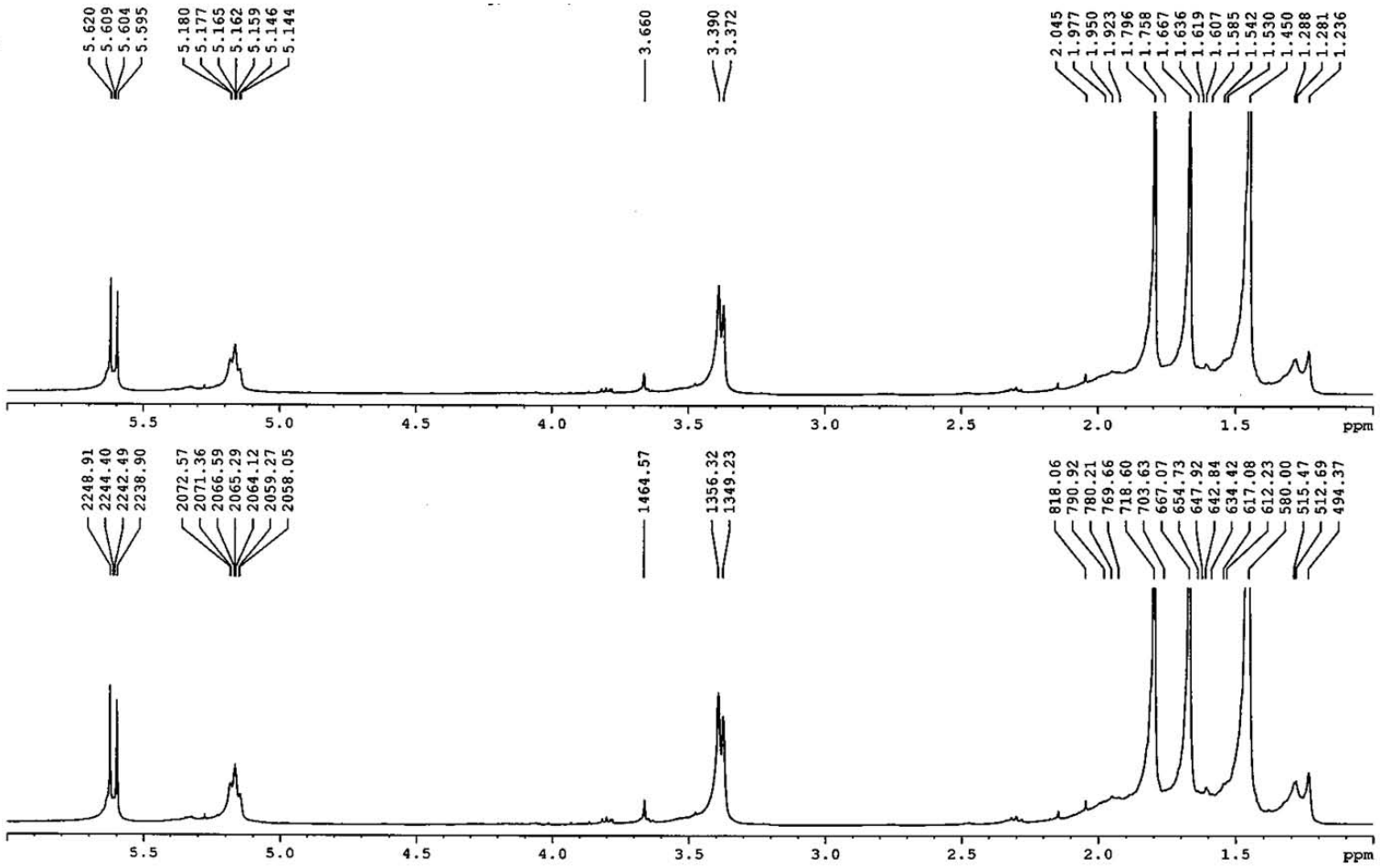


Figure 7a Expansion of ^{1}H-NMR Spectrum of Osajin (**44**) in $CDCl_3$

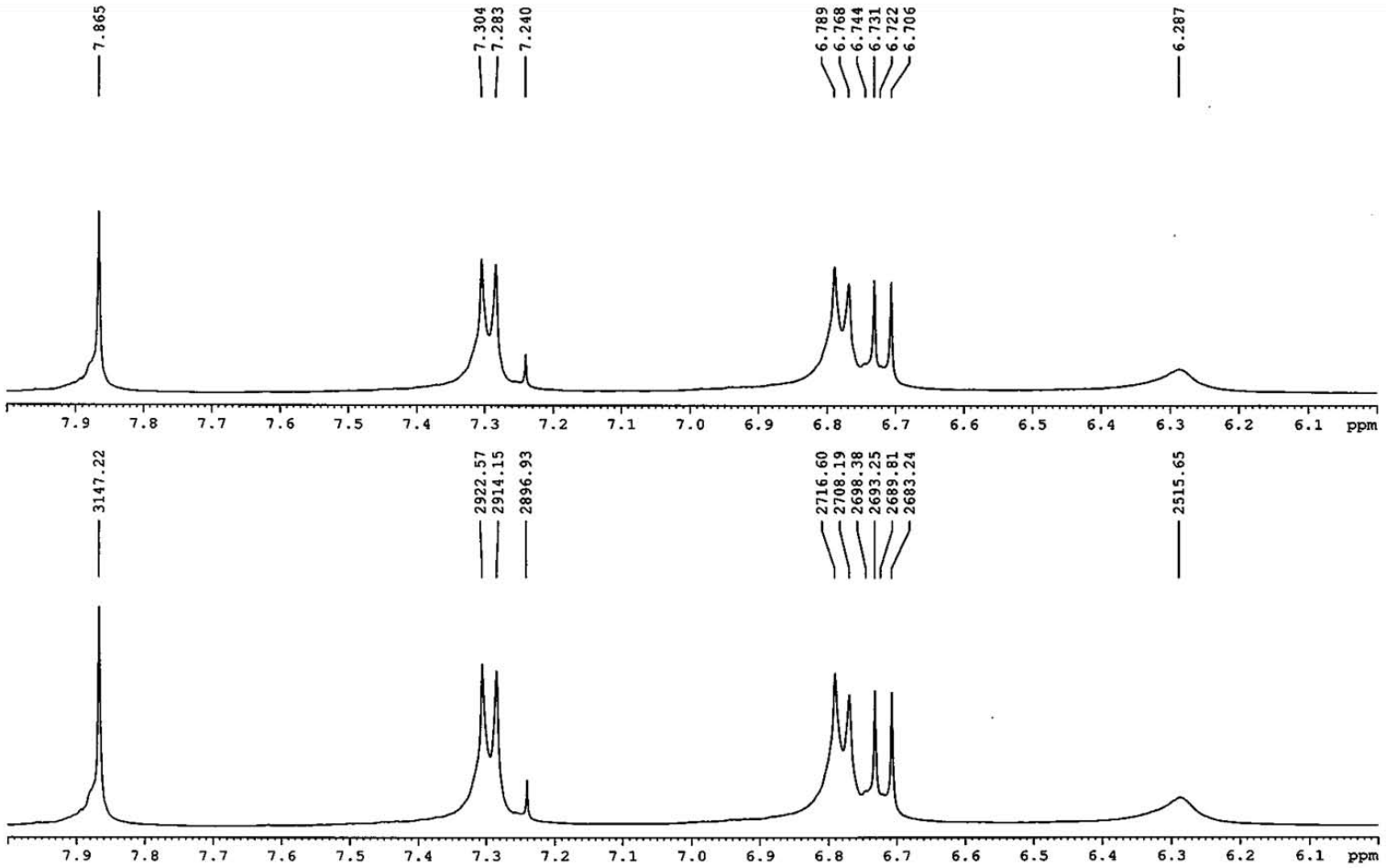


Figure 7b Expansion of ^{1}H-NMR Spectrum of Osajin (**44**) in $CDCl_3$

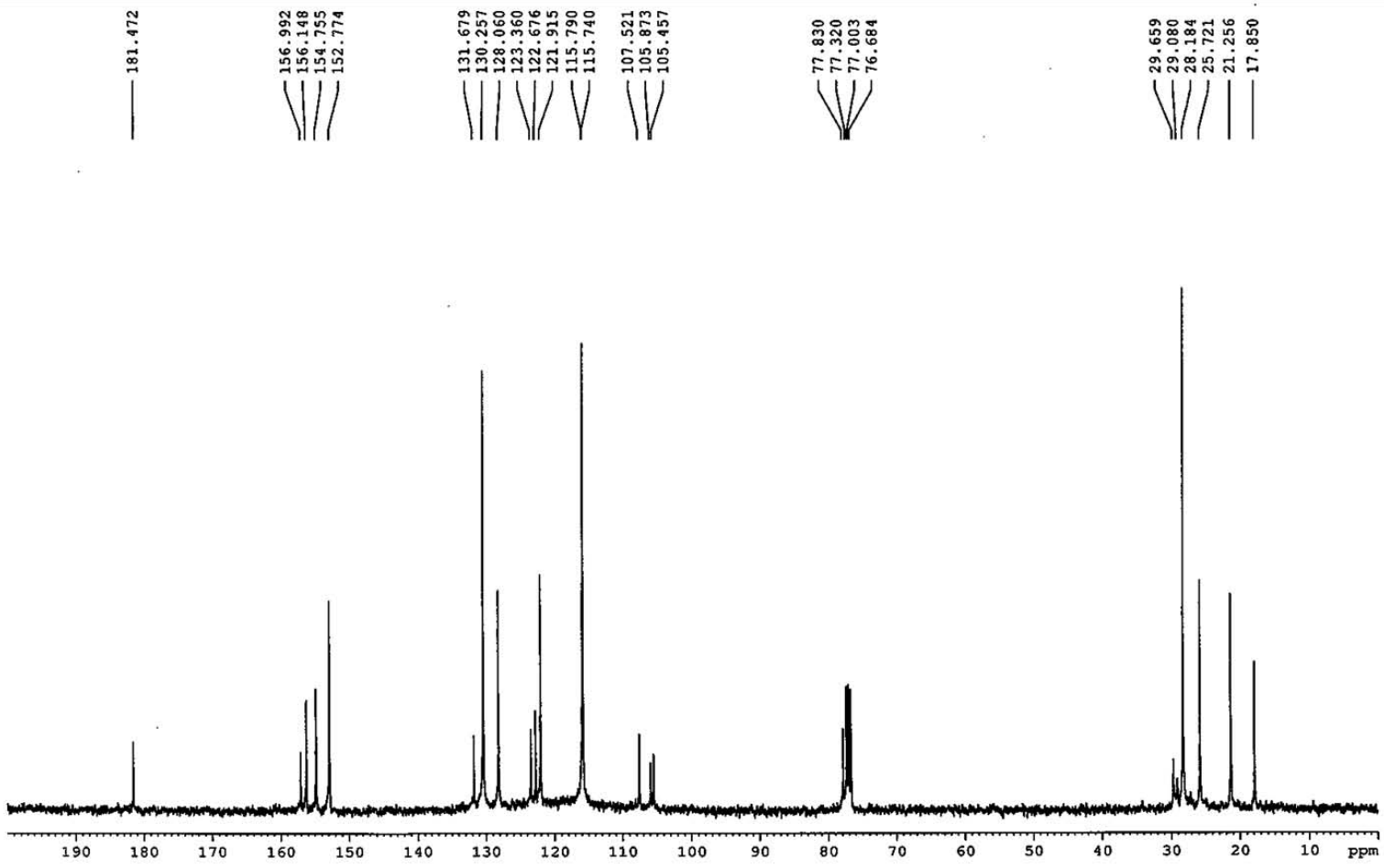


Figure 7c ^{13}C-NMR Spectrum of Osajin (**44**) in $CDCl_3$

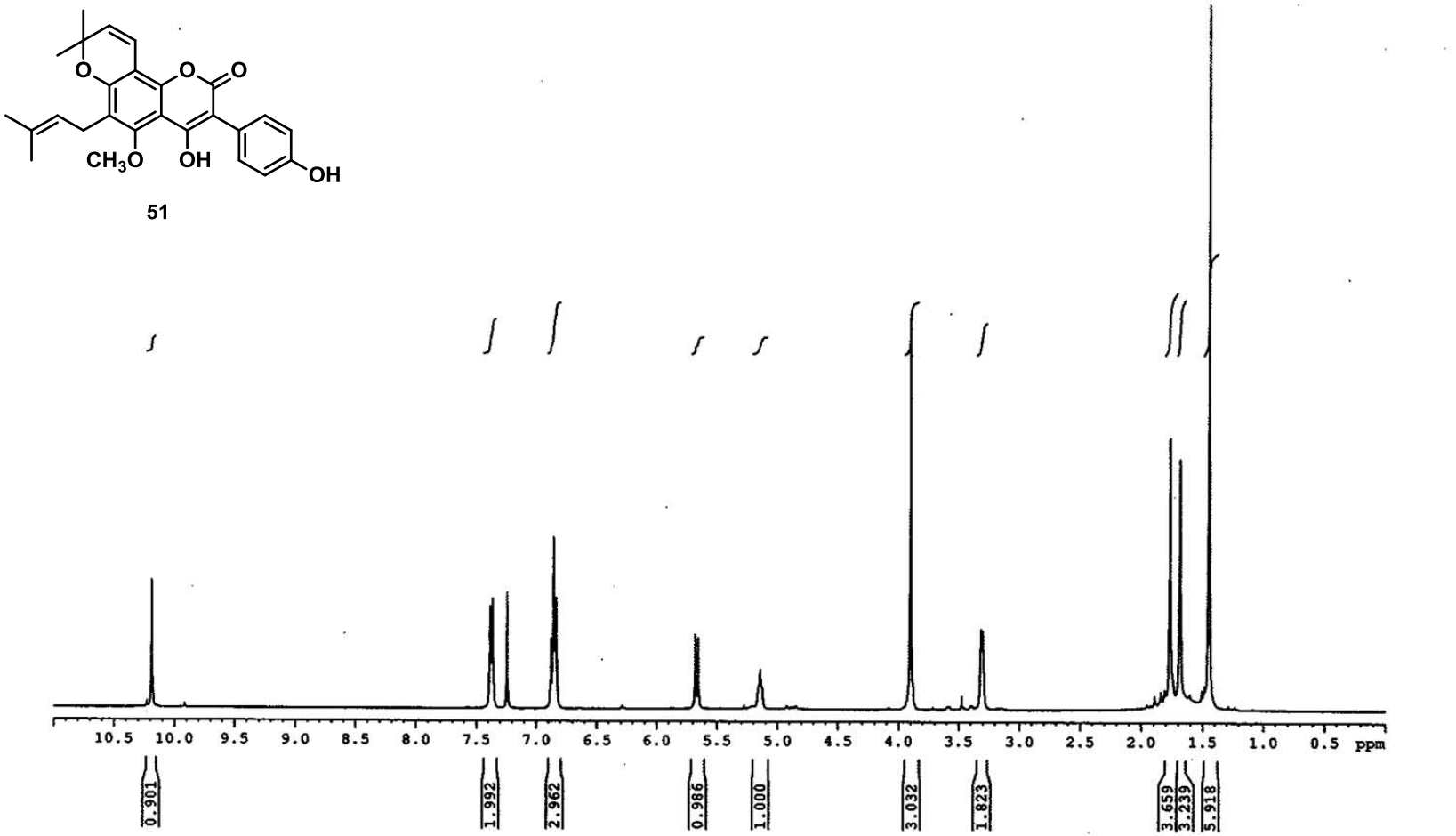


Figure 8 ^{1}H-NMR Spectrum of Scandenin (**51**) in $CDCl_3$

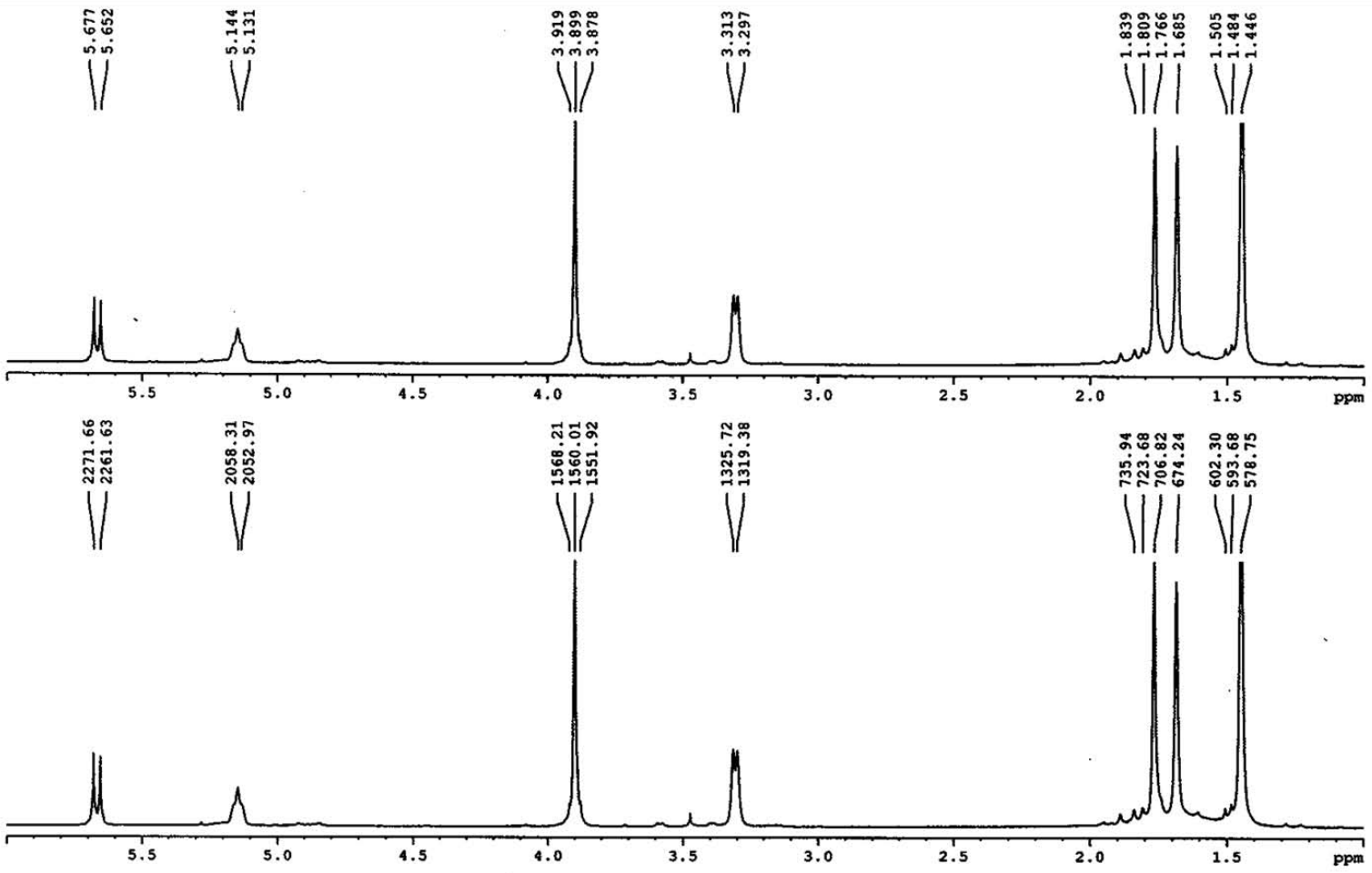


Figure 8a Expansion of ^{1}H-NMR Spectrum of Scandenin (**51**) in $CDCl_3$

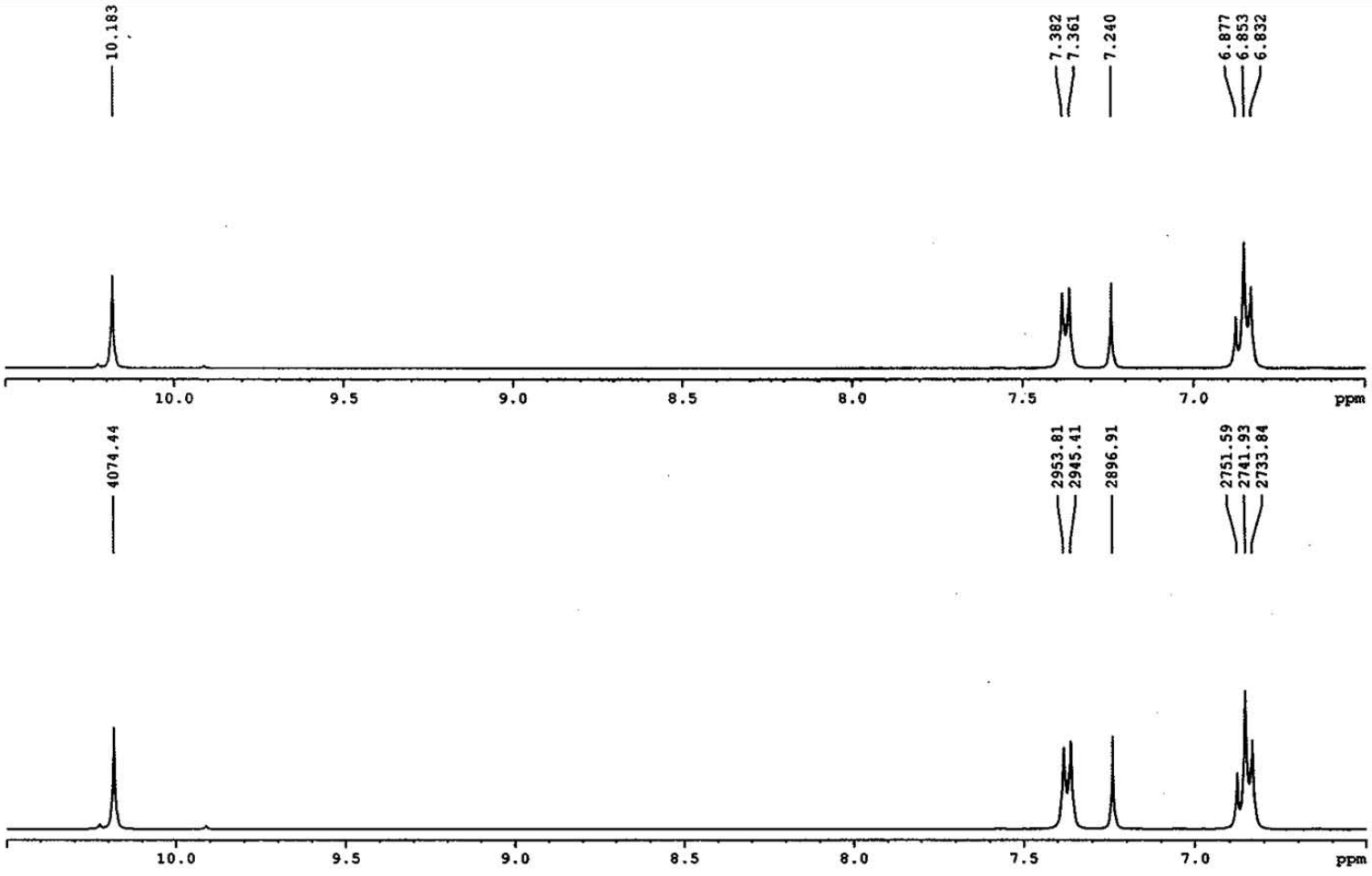


Figure 8b Expansion of ^{1}H-NMR Spectrum of Scandenin (**51**) in $CDCl_3$

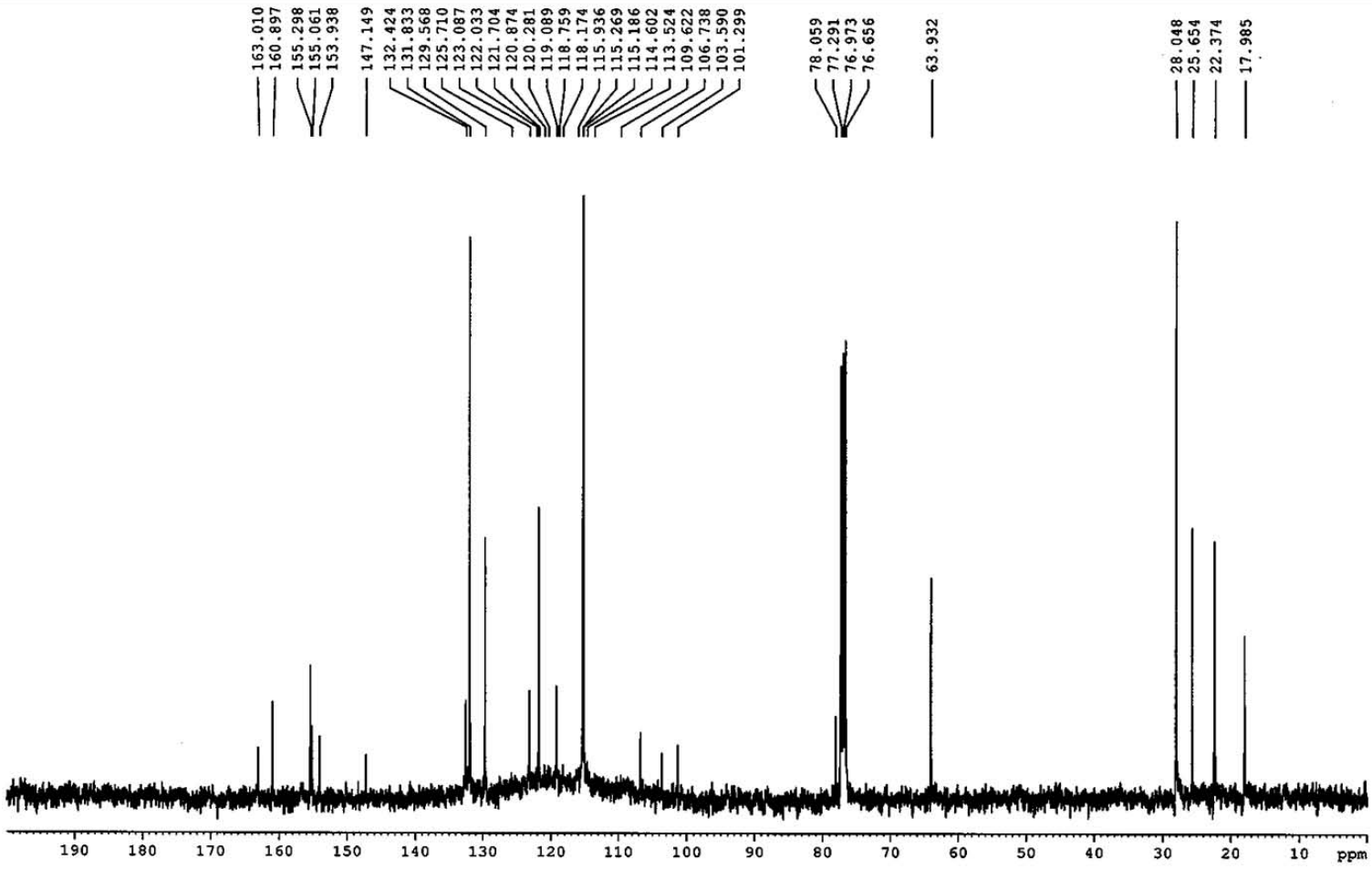


Figure 8c ^{13}C-NMR Spectrum of Scandenin (**51**) in $CDCl_3$

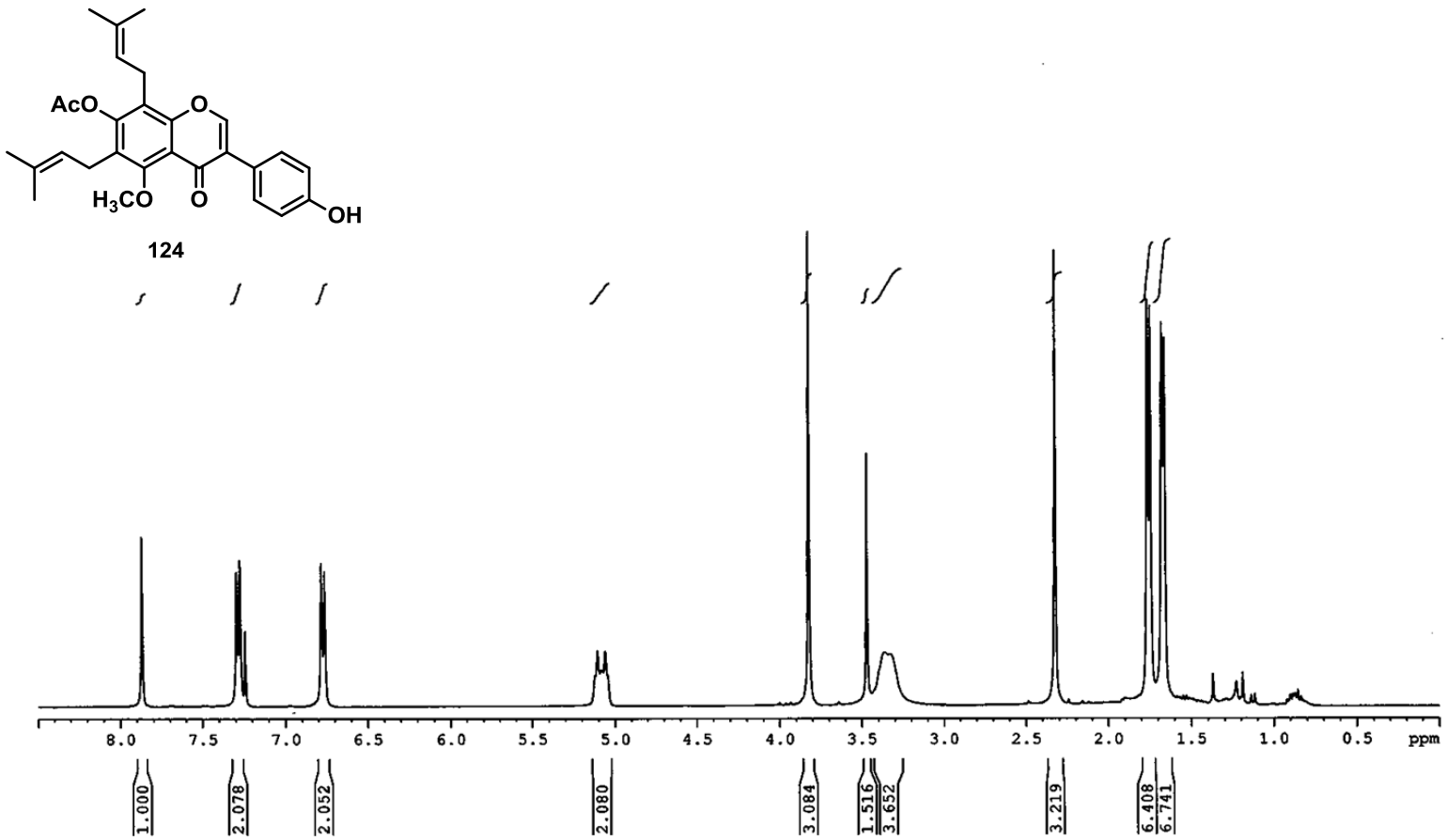


Figure 9 ^{1}H-NMR Spectrum of Derrisisoflavone A 7-*O*-acetate (**124**) in $CDCl_3$

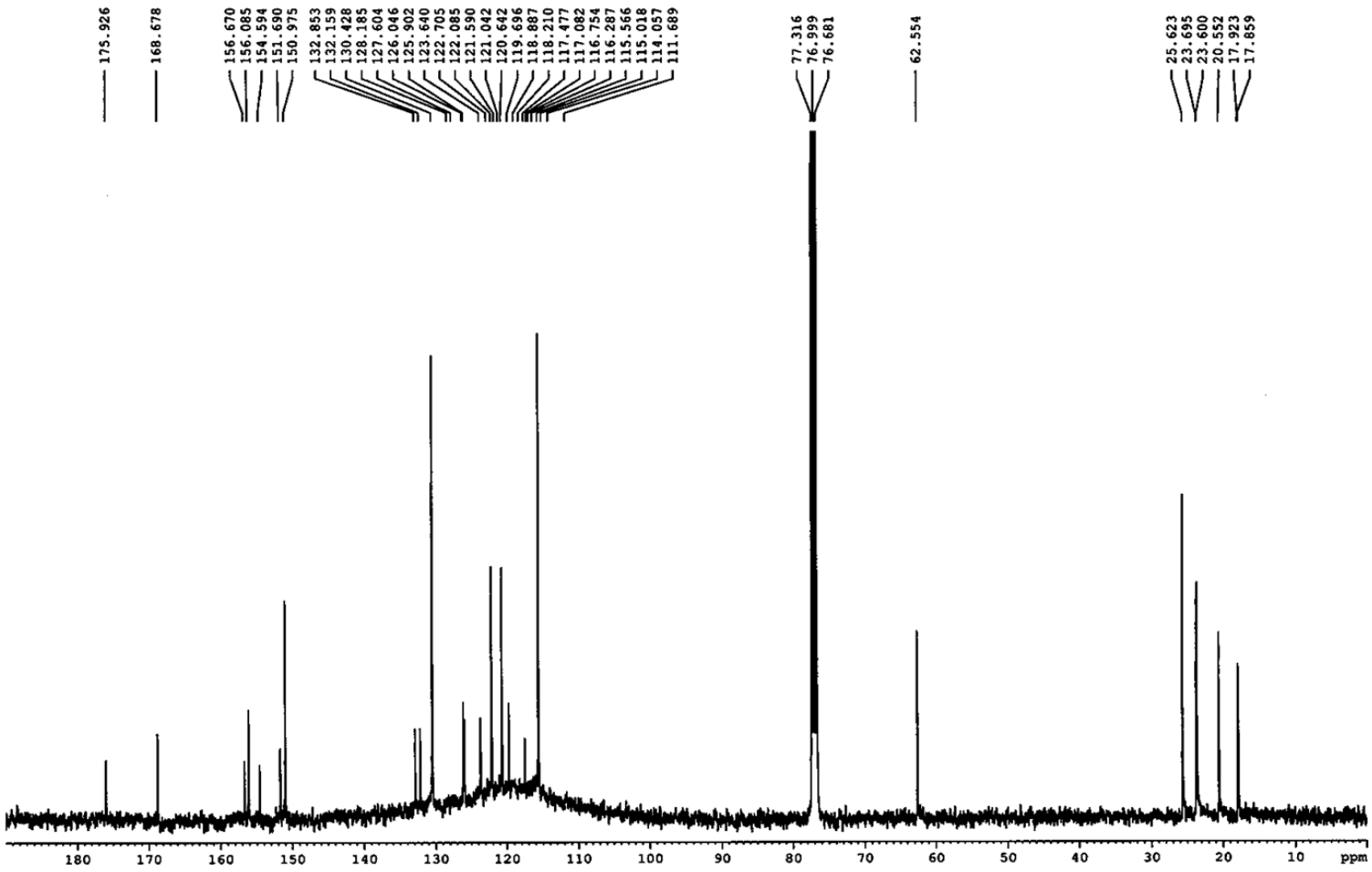


Figure 9a ^{13}C-NMR Spectrum of Derrisisoflavone A 7-*O*-acetate (**124**) in $CDCl_3$

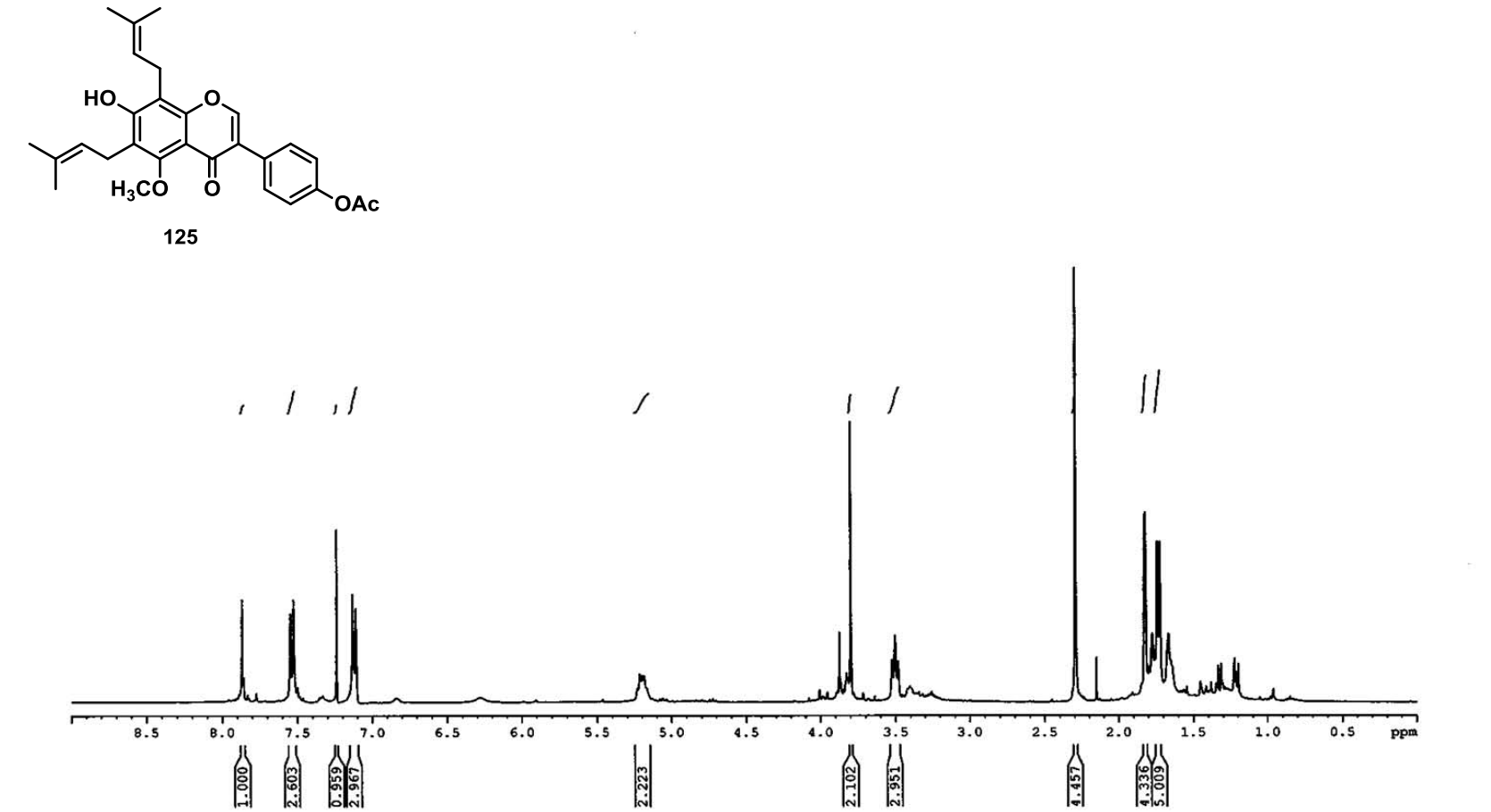


Figure 10 ^{1}H-NMR Spectrum of Derrisisoflavone A 4′-*O*-acetate (**125**) in $CDCl_3$

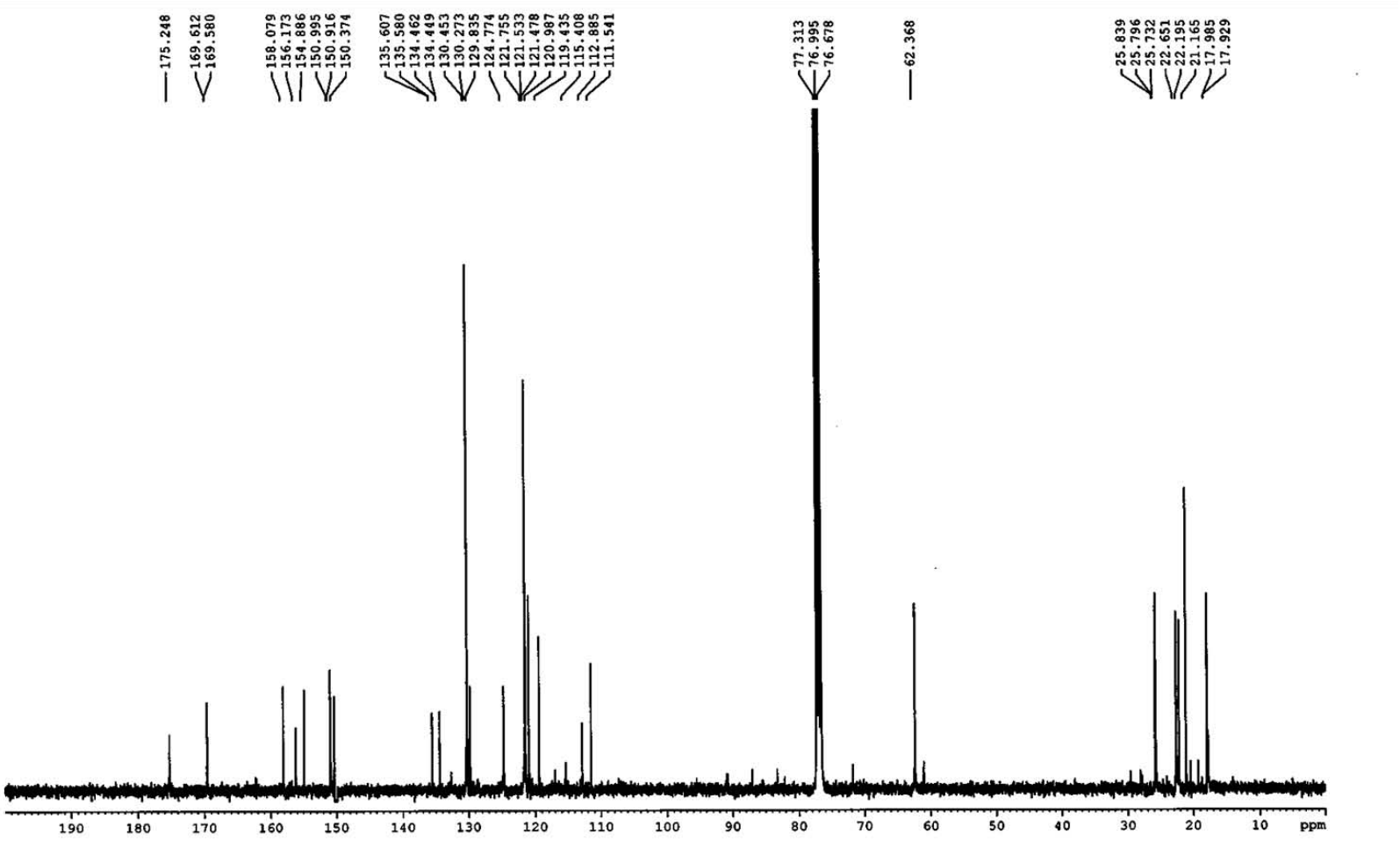


Figure 10a ^{13}C-NMR Spectrum of Derrisisoflavone A 4′-*O*-acetate (**125**) in $CDCl_3$

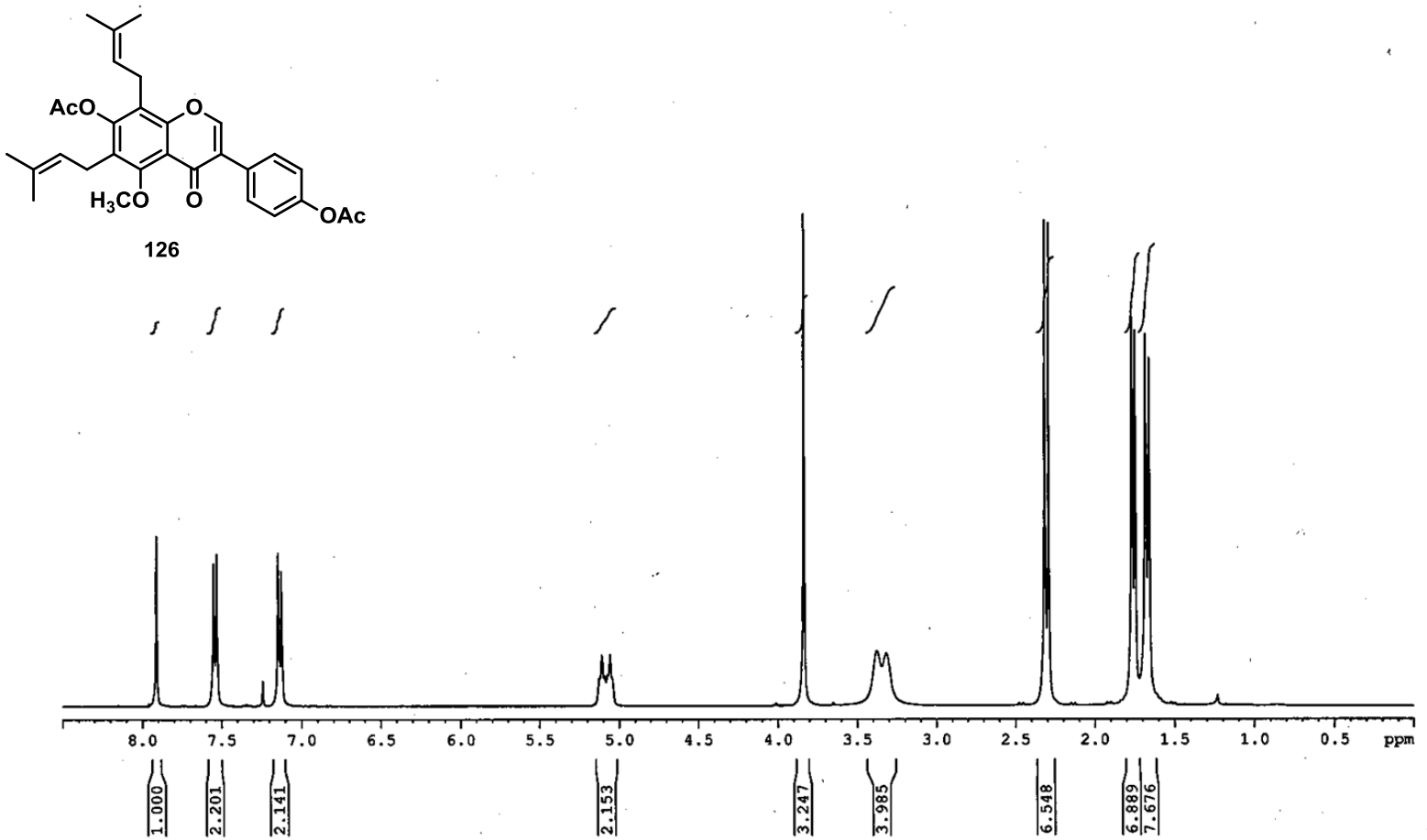


Figure 11 ^{1}H-NMR Spectrum of Derrisisoflavone A 7,4′-di-*O*-diacetate (**126**) in $CDCl_3$

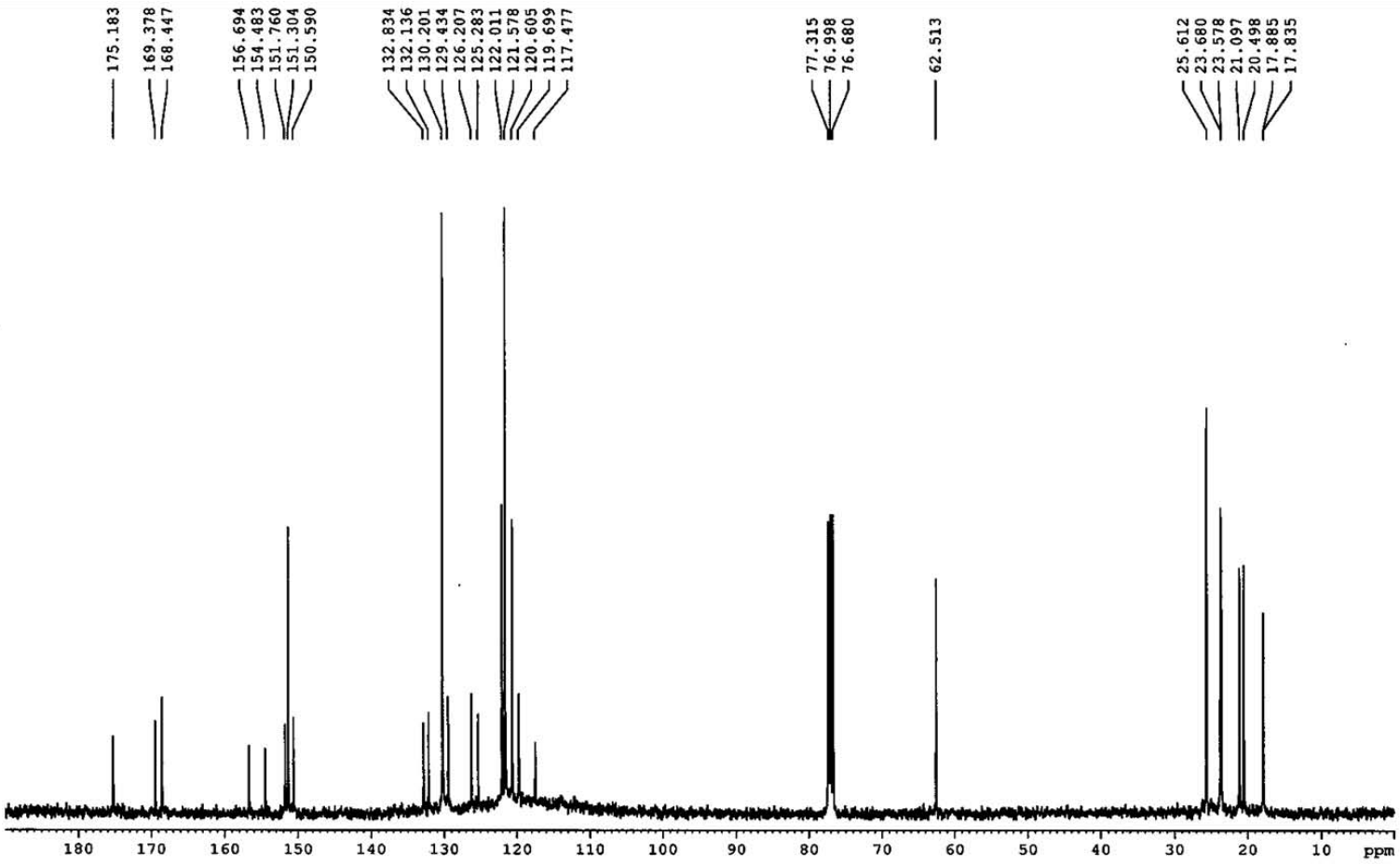
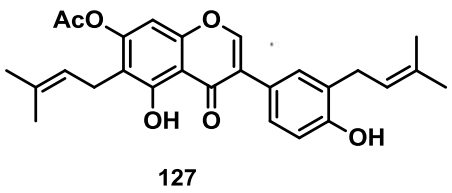


Figure 11a ^{13}C-NMR Spectrum of Derrisisoflavone A 7,4′-di-*O*-acetate (**126**) in $CDCl_3$



127

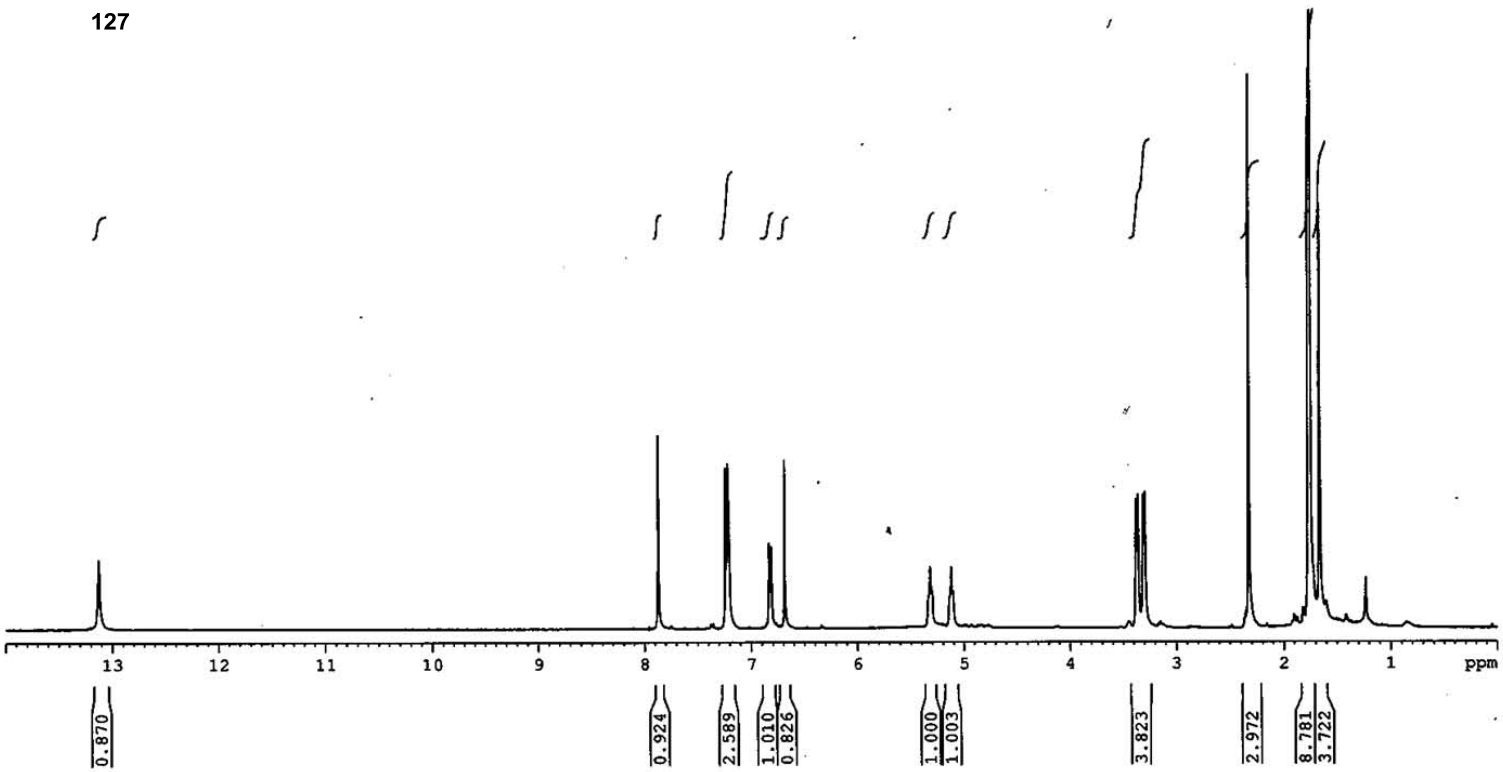


Figure 12 ^{1}H-NMR Spectrum of Lupalbigenin 7-*O*-acetate (**127**) in $CDCl_3$

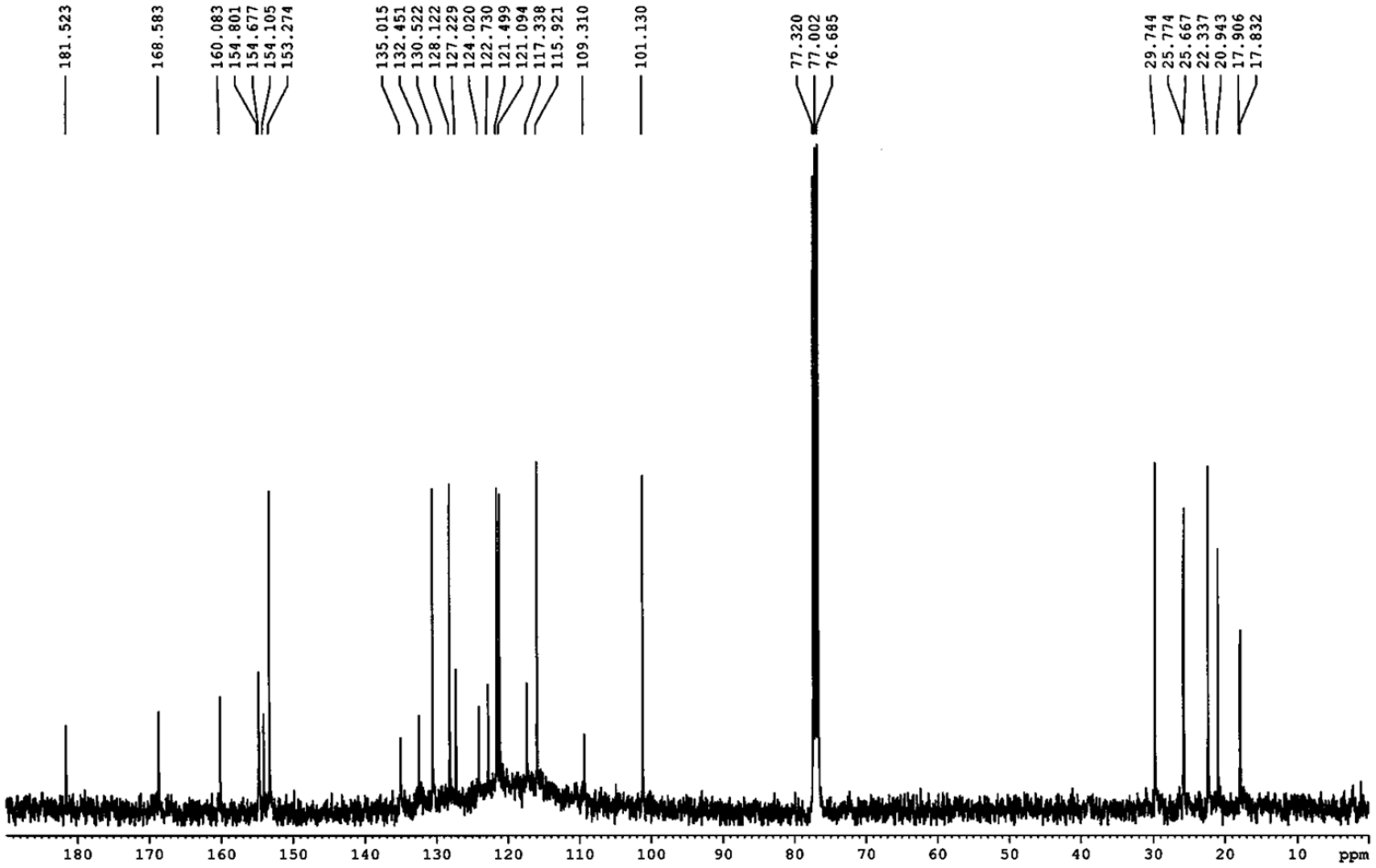


Figure 12a ^{13}C-NMR Spectrum of Lupalbigenin 7-*O*-acetate (**127**) in $CDCl_3$

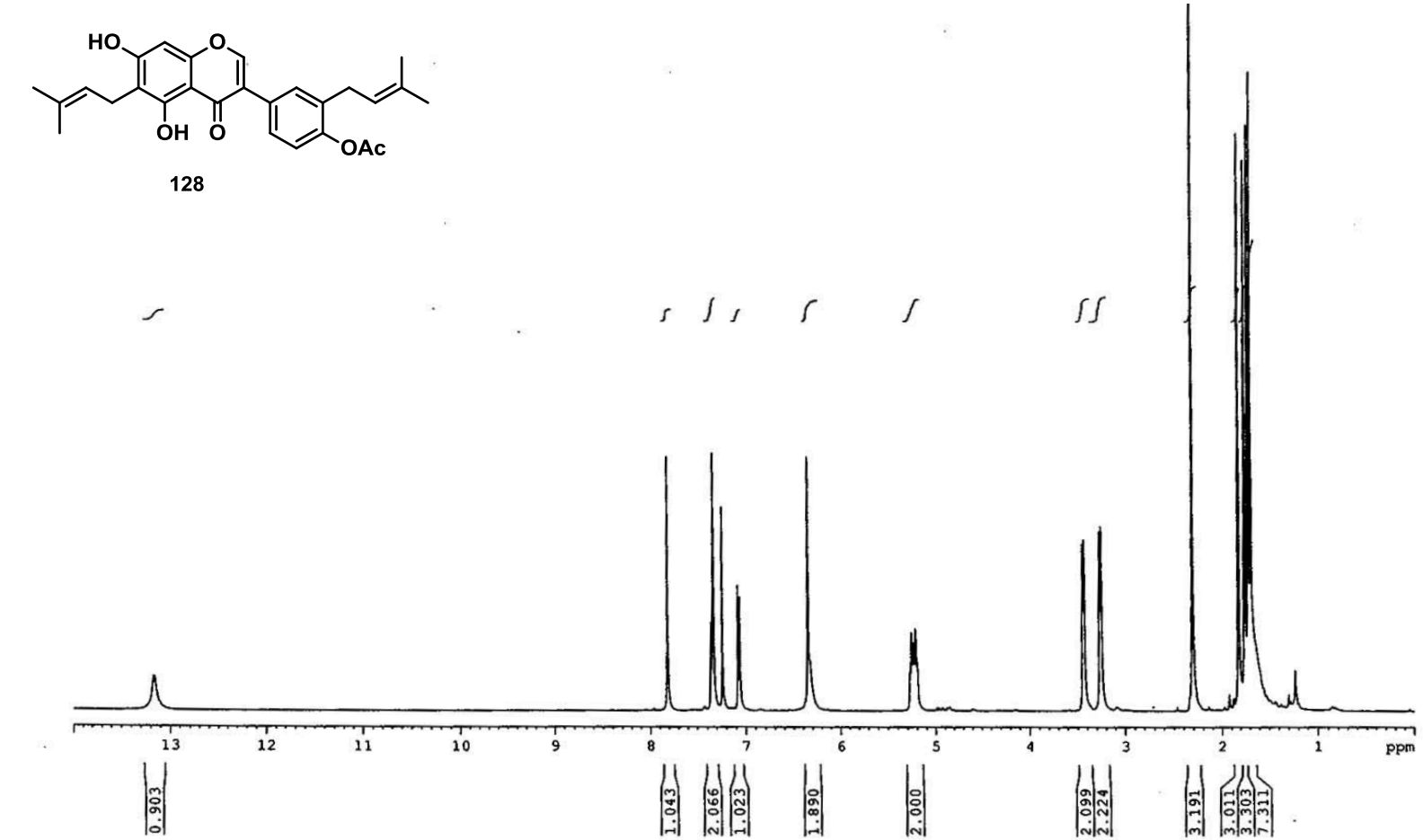


Figure 13 ^{1}H-NMR Spectrum of Lupalbigenin 4′-*O*-acetate (**128**) in $CDCl_3$

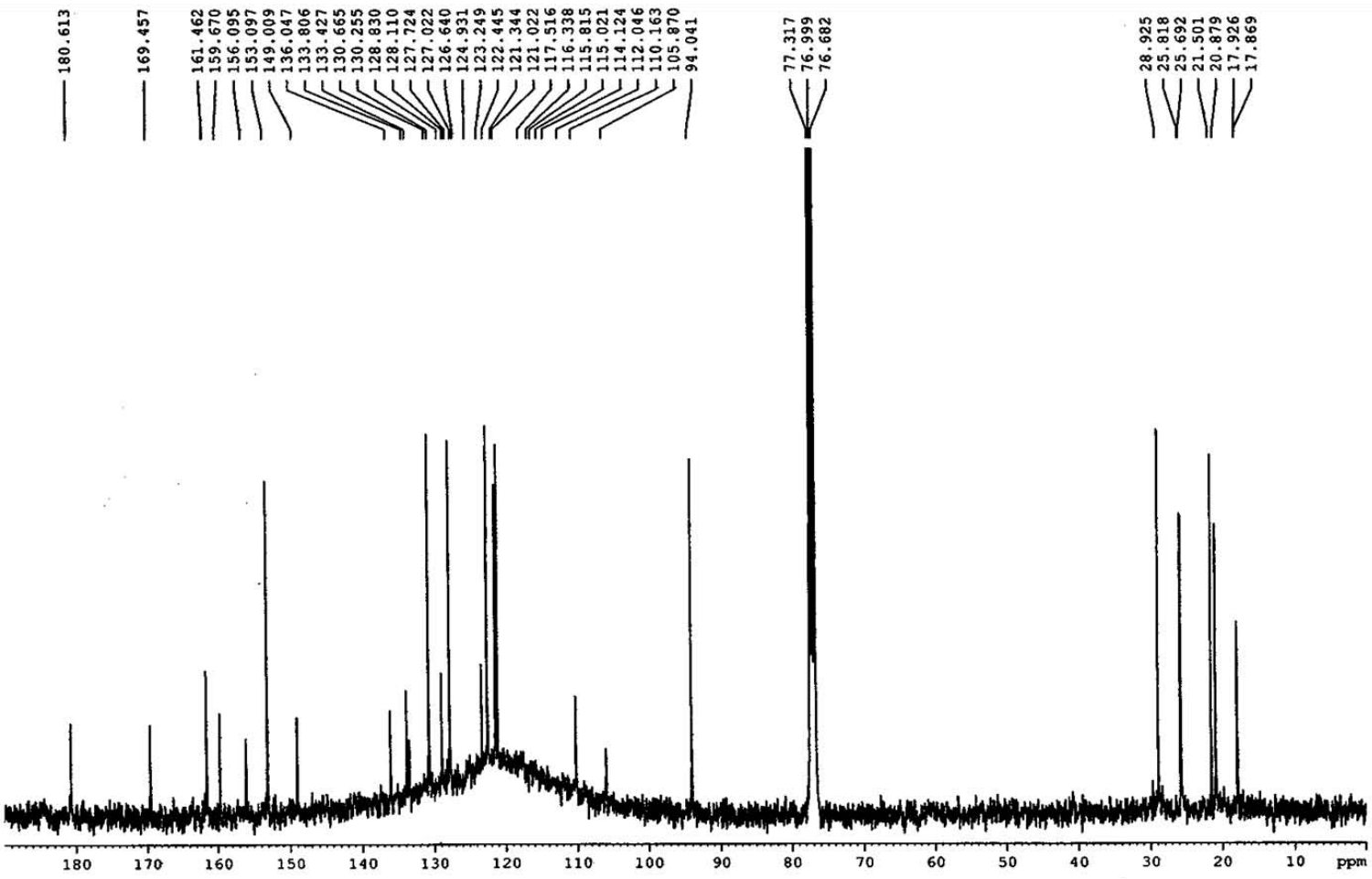


Figure 13a ^{13}C-NMR Spectrum of Lupalbigenin 4′-*O*-acetate (**128**) in $CDCl_3$

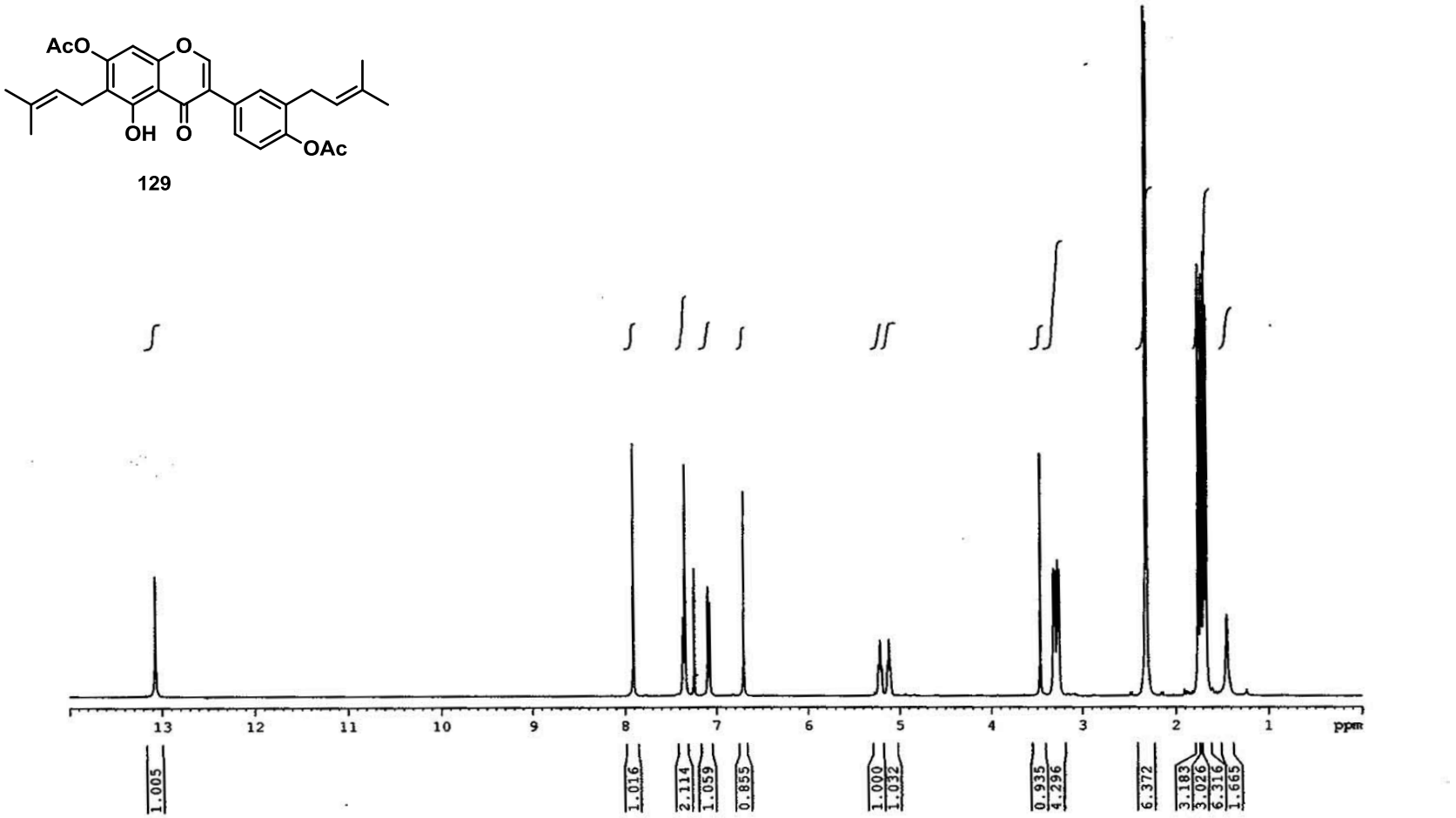


Figure 14 ^{1}H-NMR Spectrum of Lupalbigenin 7,4′-di-*O*-acetate (**129**) in $CDCl_3$

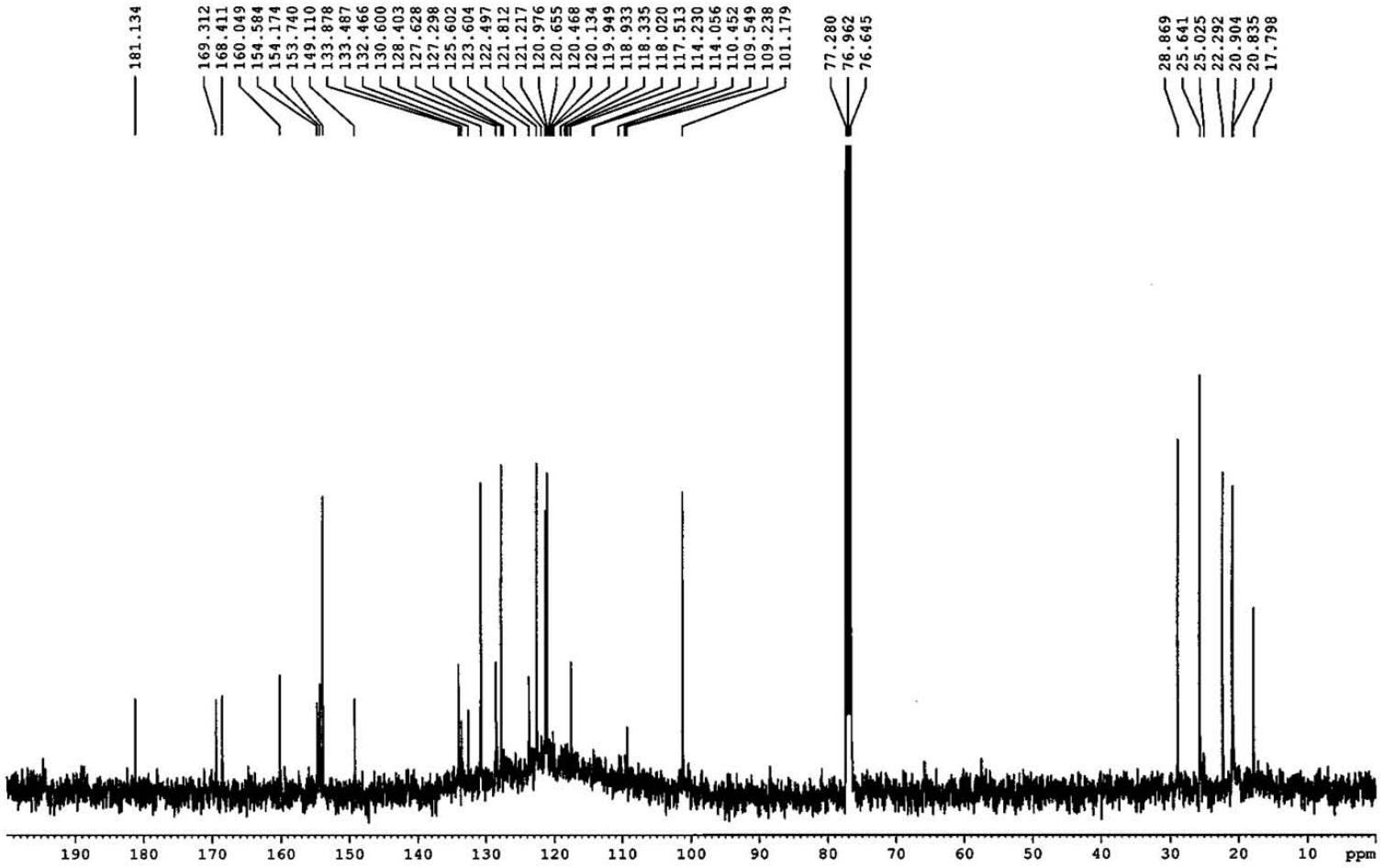


Figure 14a ^{13}C-NMR Spectrum of Lupalbigenin 7,4′-di-*O*-acetate (**129**) in $CDCl_3$

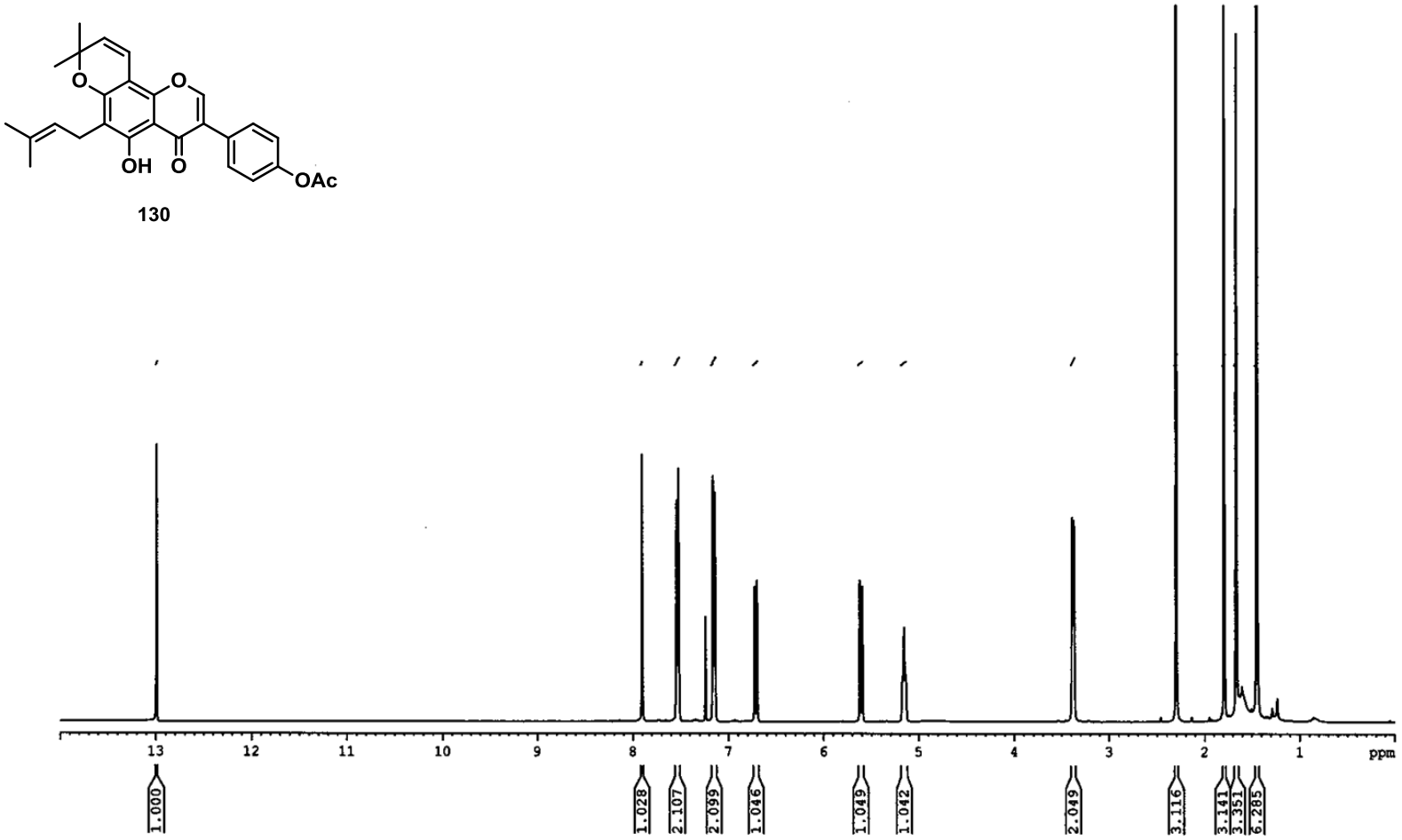


Figure 15 ^{1}H-NMR Spectrum of Osajin 4′-*O*-acetate (**130**) in $CDCl_3$

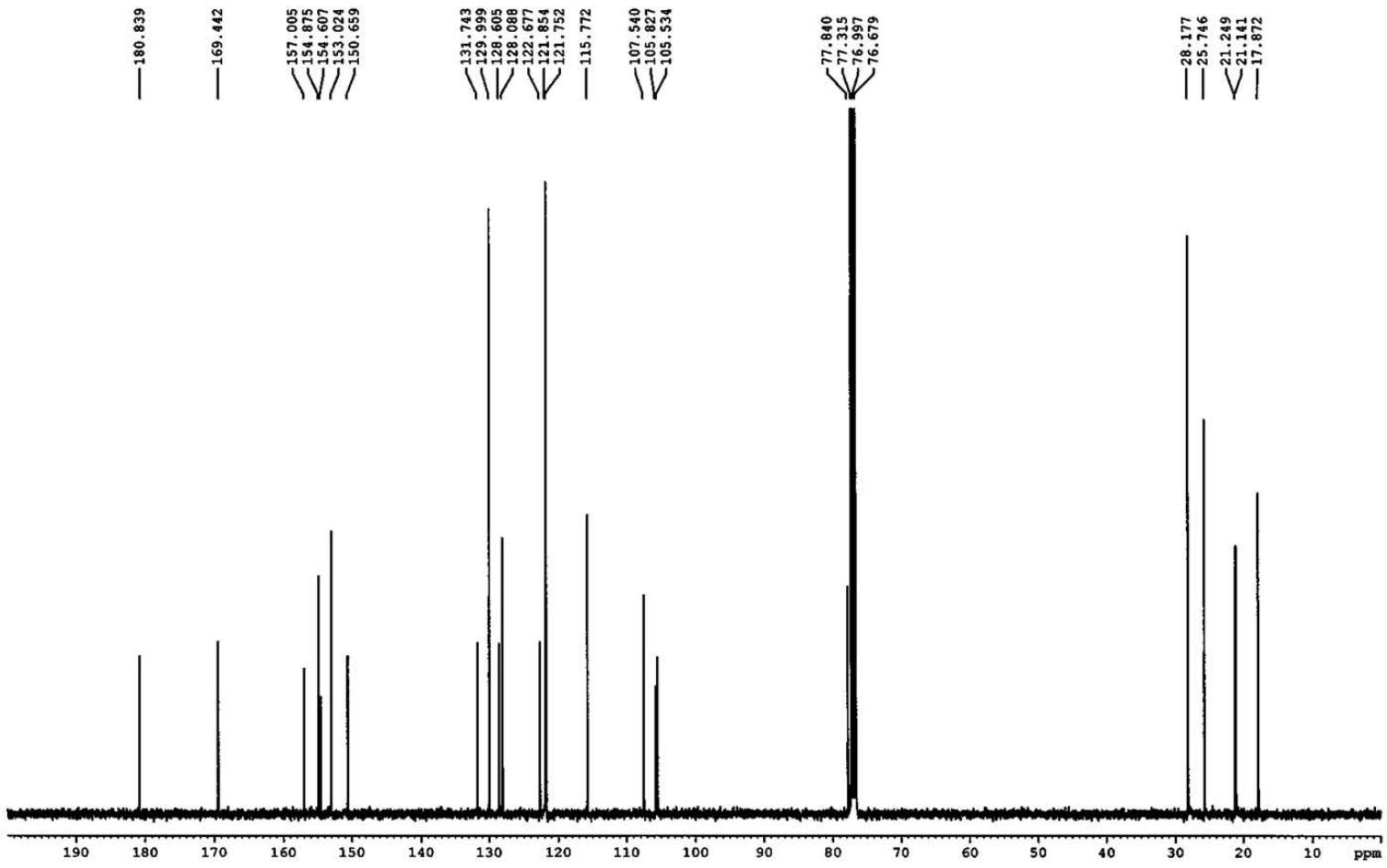


Figure 15a ^{13}C-NMR Spectrum of Osajin 4′-*O*-acetate (**130**) in $CDCl_3$

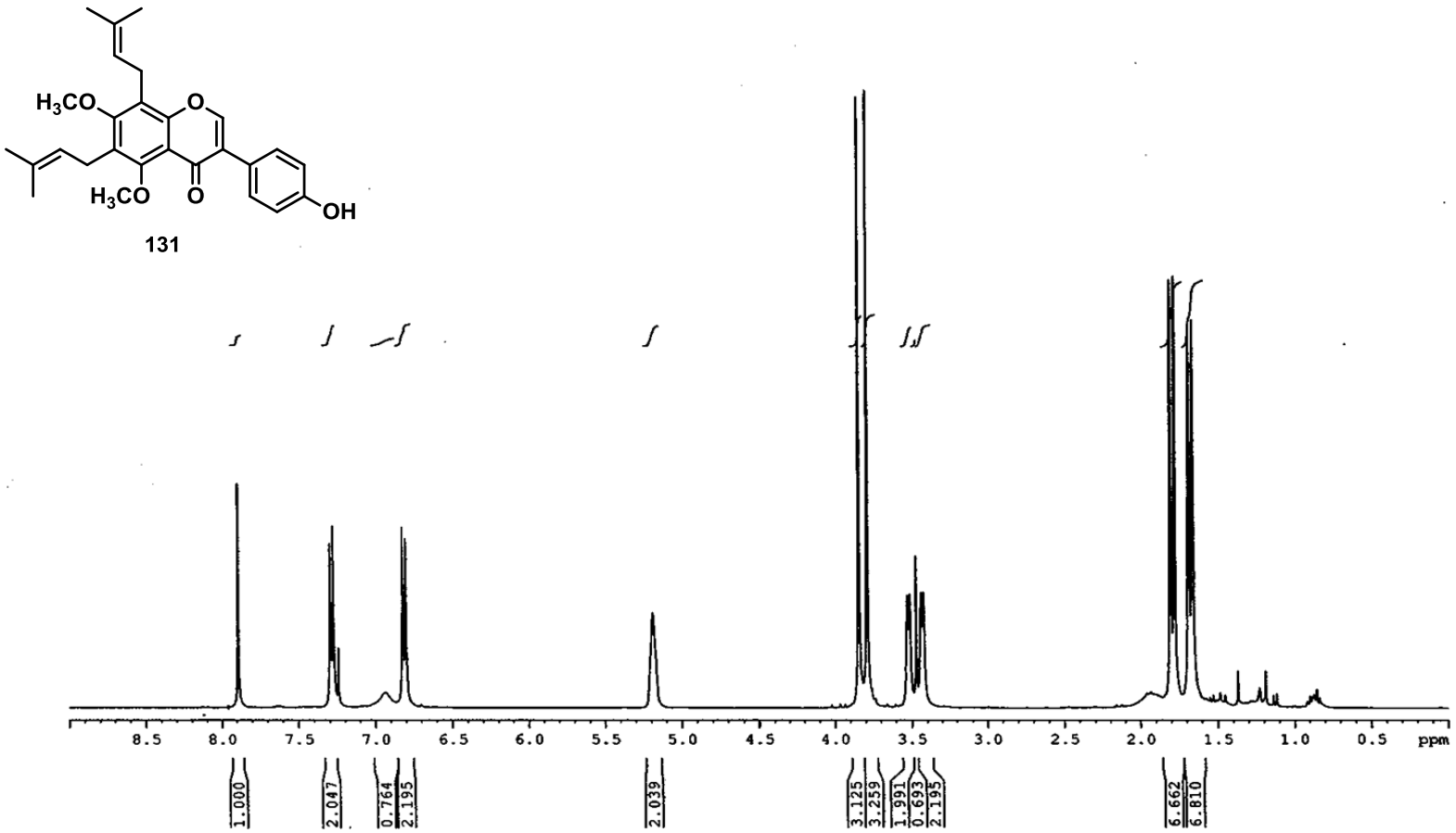


Figure 16 ^{1}H-NMR Spectrum of Derrisisoflavone A 7-*O*-methyl ether (**131**) in $CDCl_3$

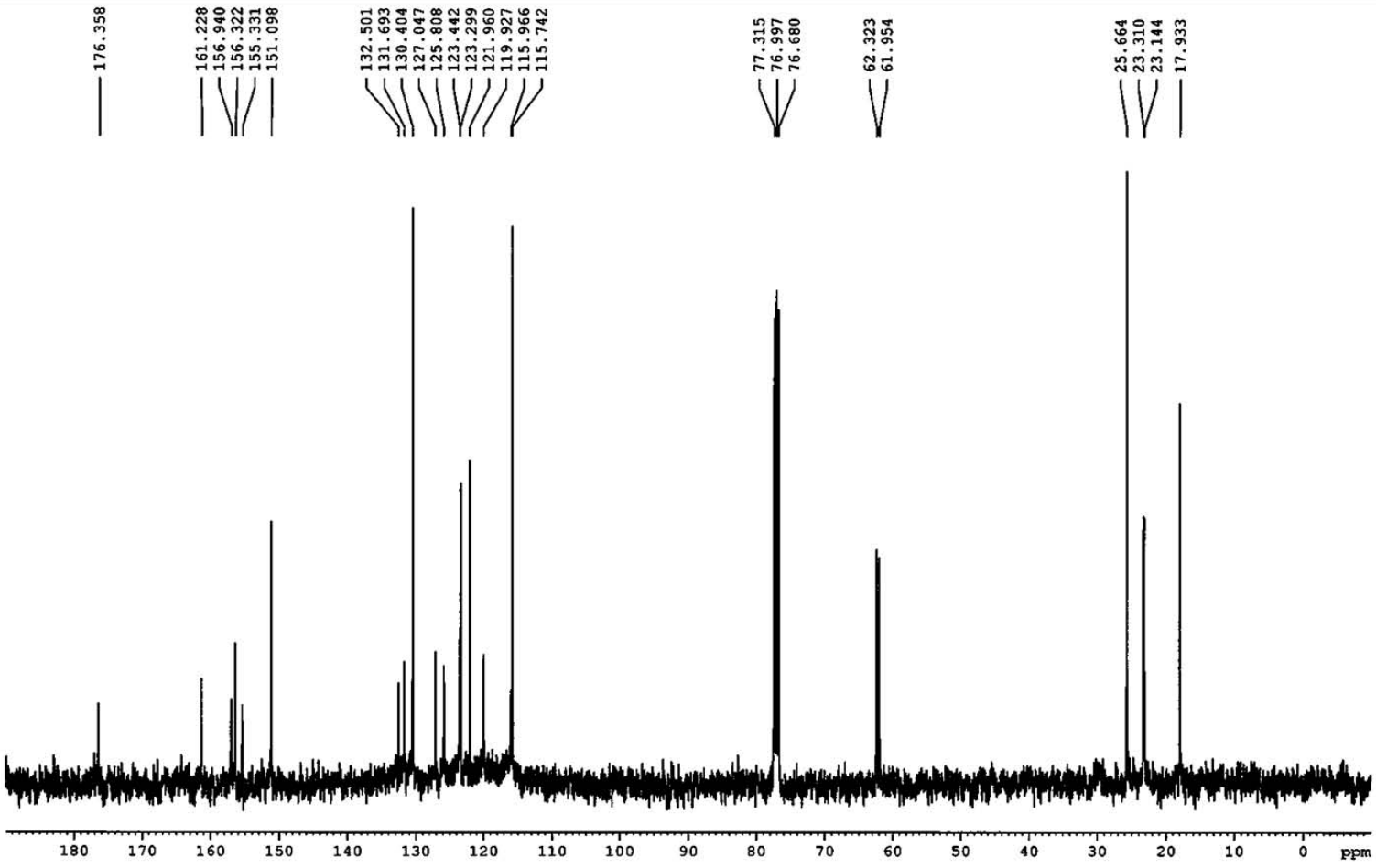
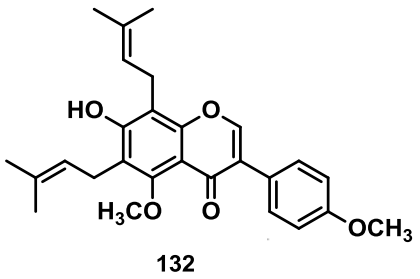


Figure 16a ^{13}C-NMR Spectrum of Derrisisoflavone A 7-*O*-methyl ether (**131**) in $CDCl_3$



132

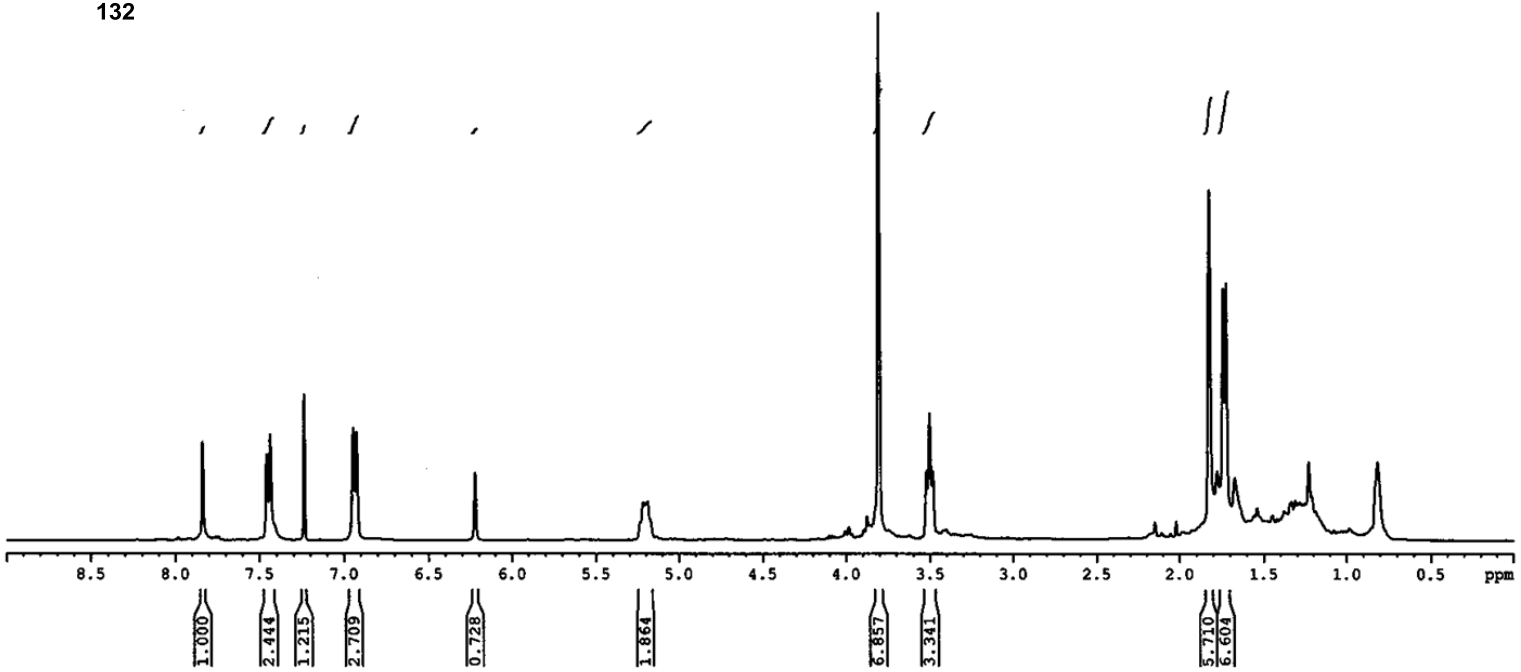


Figure 17 ^{1}H-NMR Spectrum of Derrisisoflavone A 4′-*O*-methyl ether (**132**) in $CDCl_3$

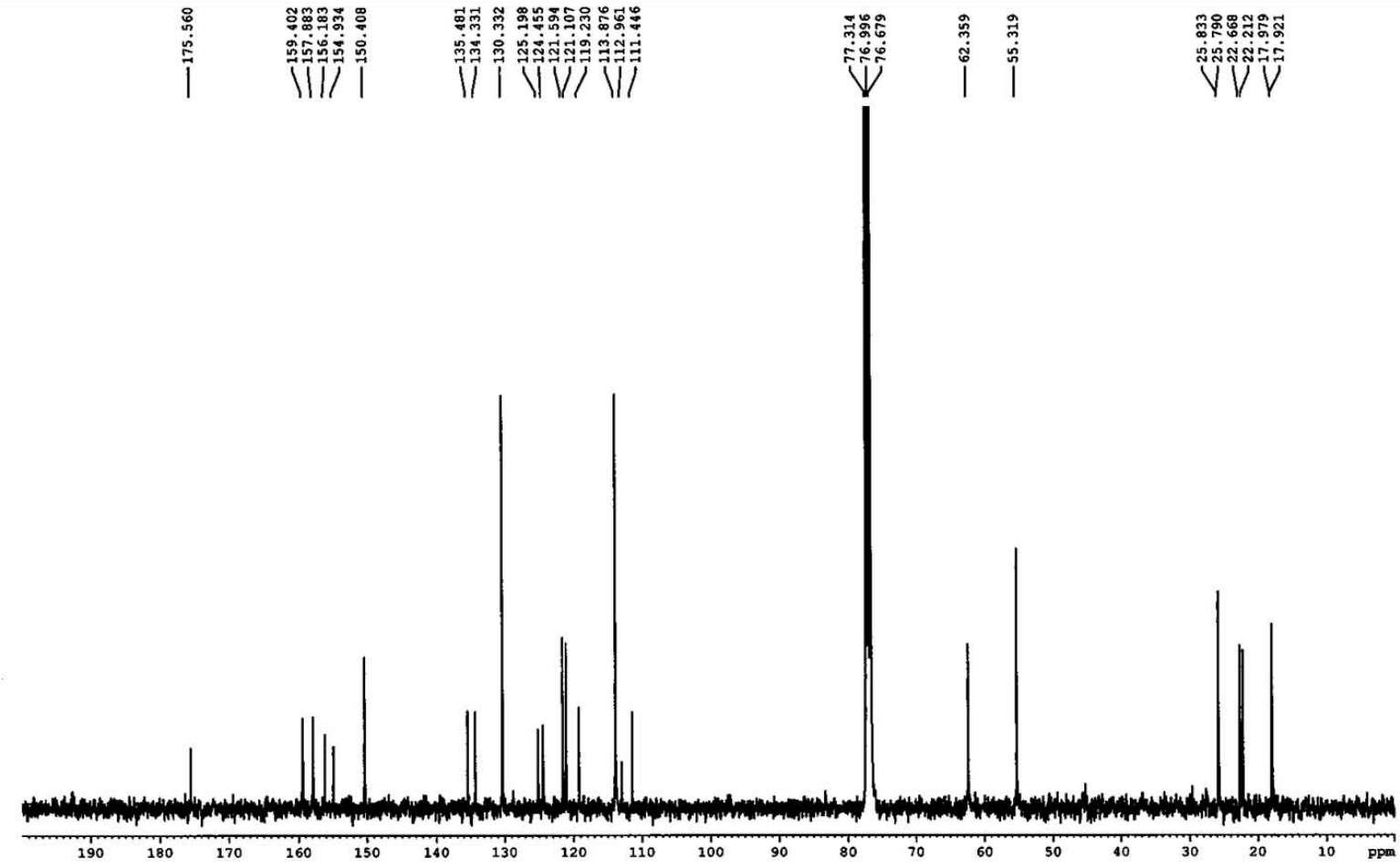


Figure 17a ^{13}C-NMR Spectrum of Derrisisoflavone A 4′-*O*-methyl ether (**132**) in $CDCl_3$

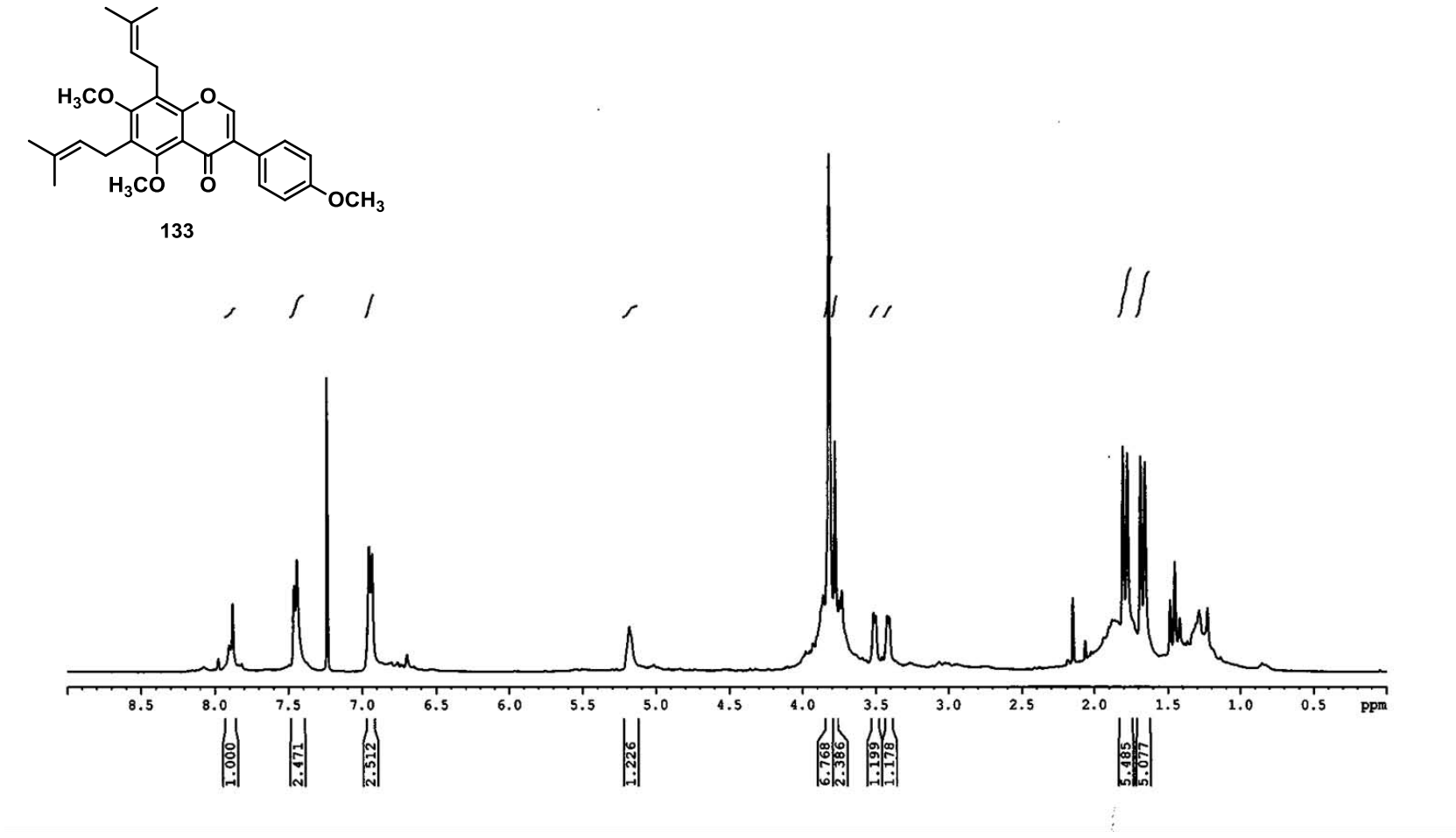


Figure 18 ^{1}H-NMR Spectrum of Derrisisoflavone A 7,4′-di-*O*-methyl ether (**133**) in $CDCl_3$

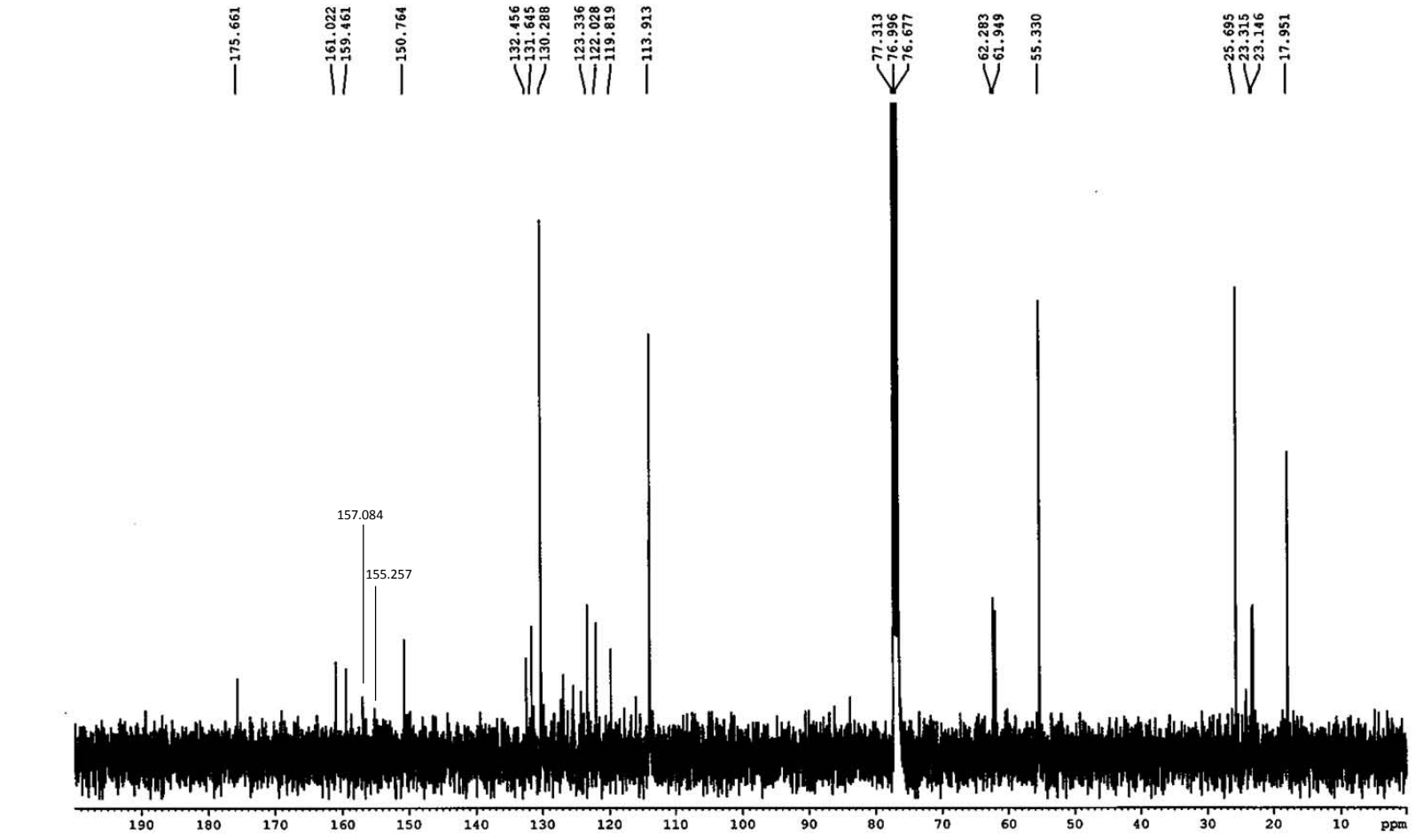
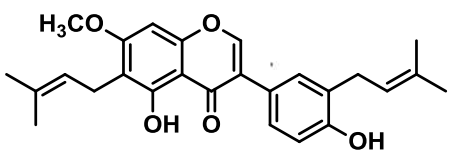


Figure 18a ^{13}C-NMR Spectrum of Derrisisoflavone A 7,4′-di-*O*-methyl ether (**133**) in $CDCl_3$



134

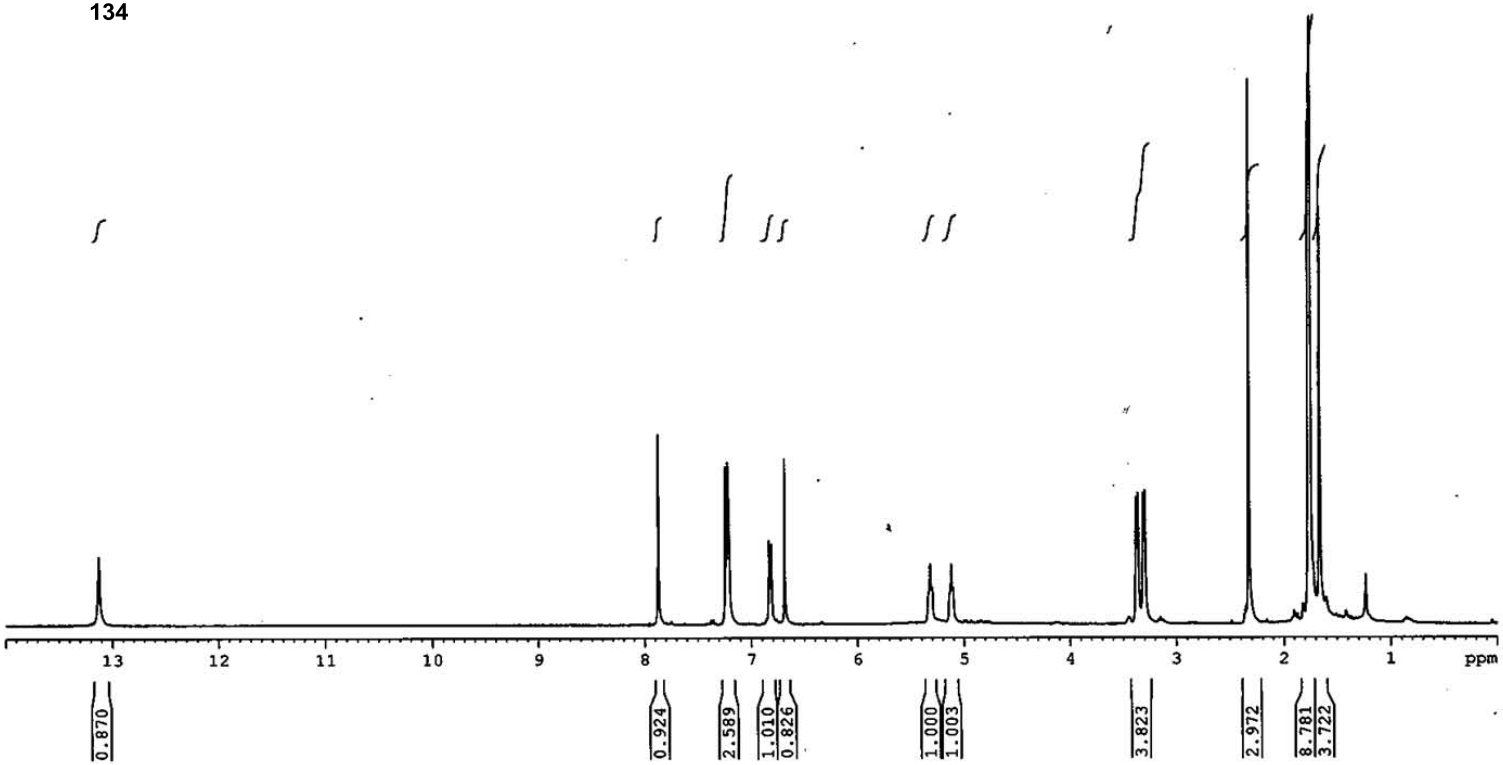


Figure 19 ^{1}H-NMR Spectrum of Lupalbigenin 7-*O*-methyl ether (**134**) in $CDCl_3$

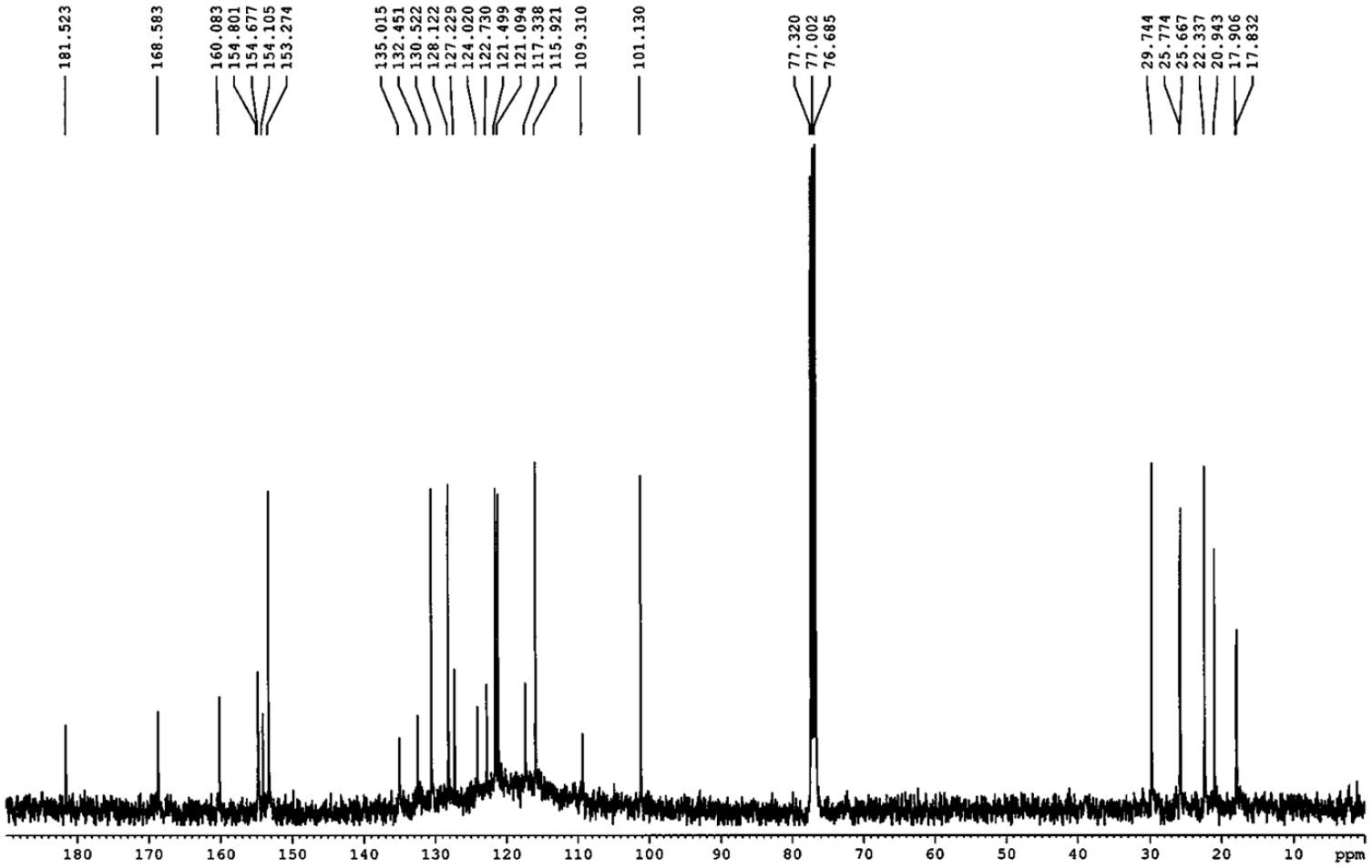


Figure 19a ^{13}C-NMR Spectrum of Lupalbigenin 7-*O*-methyl ether (**134**) in $CDCl_3$

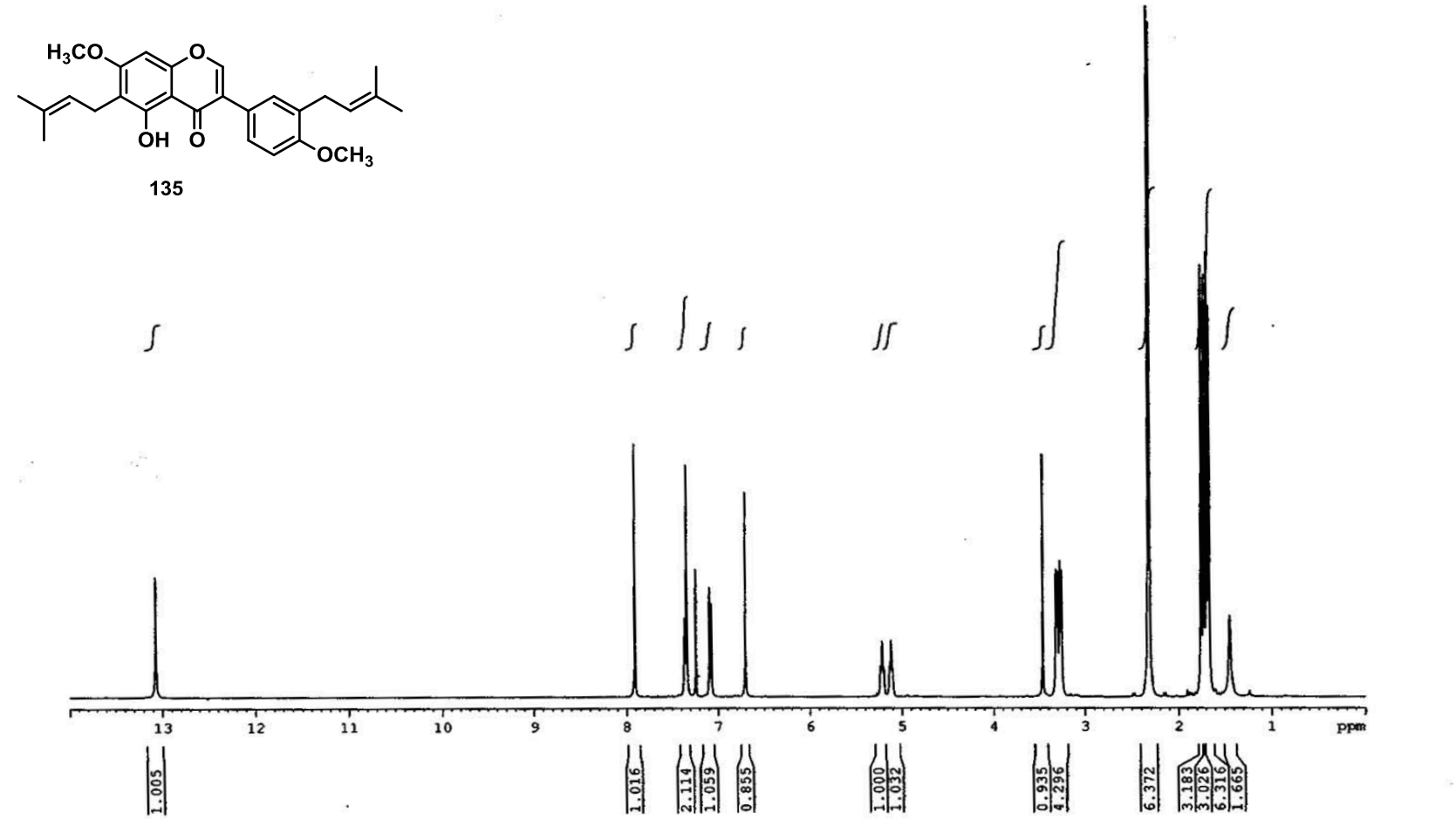


Figure 20 ^{1}H-NMR Spectrum of Lupalbigenin 7,4′-di-*O*-methyl ether (**135**) in $CDCl_3$

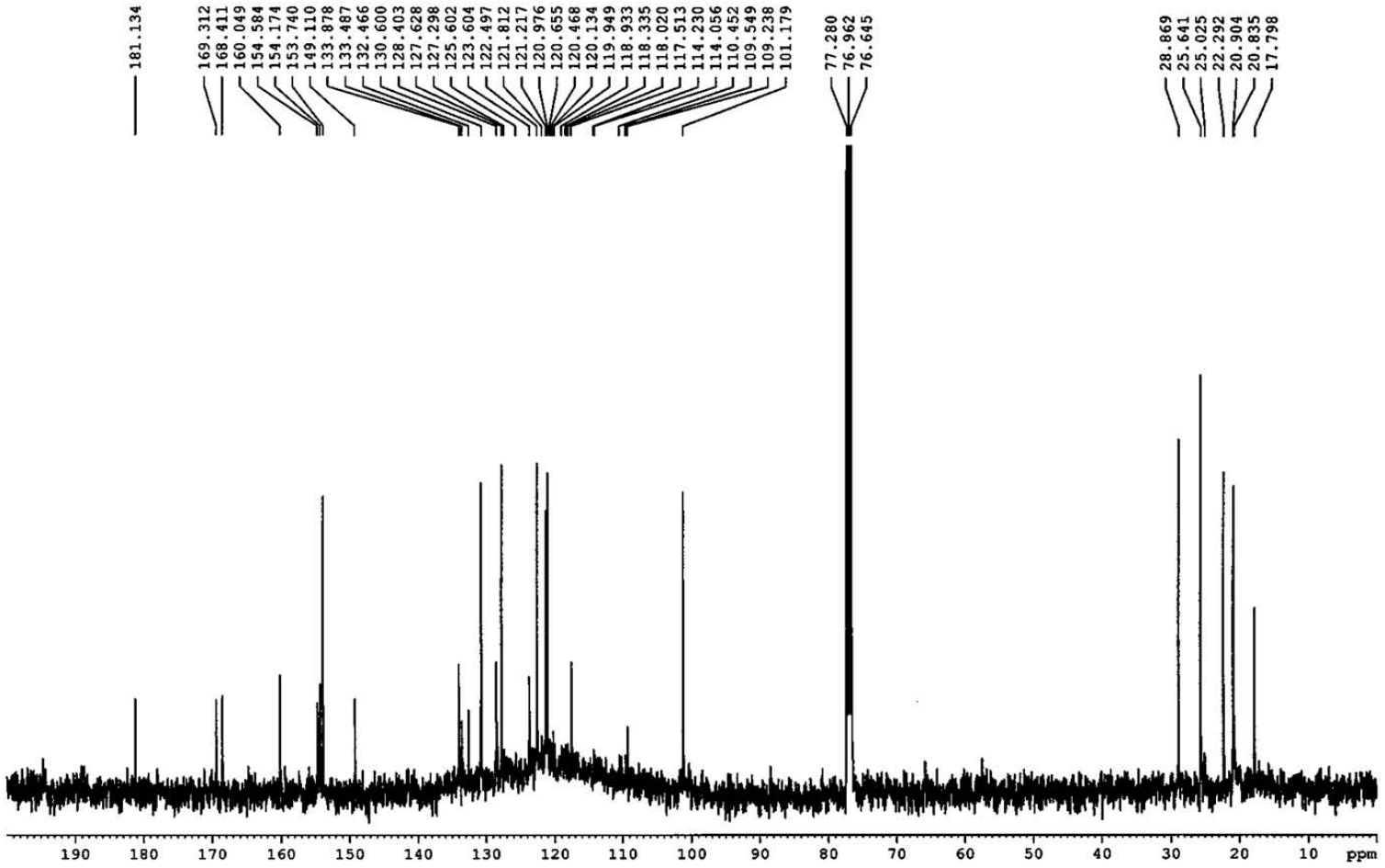


Figure 20a ^{13}C-NMR Spectrum of Lupalbigenin 7,4′-di-*O*-methyl ether (**135**) in $CDCl_3$

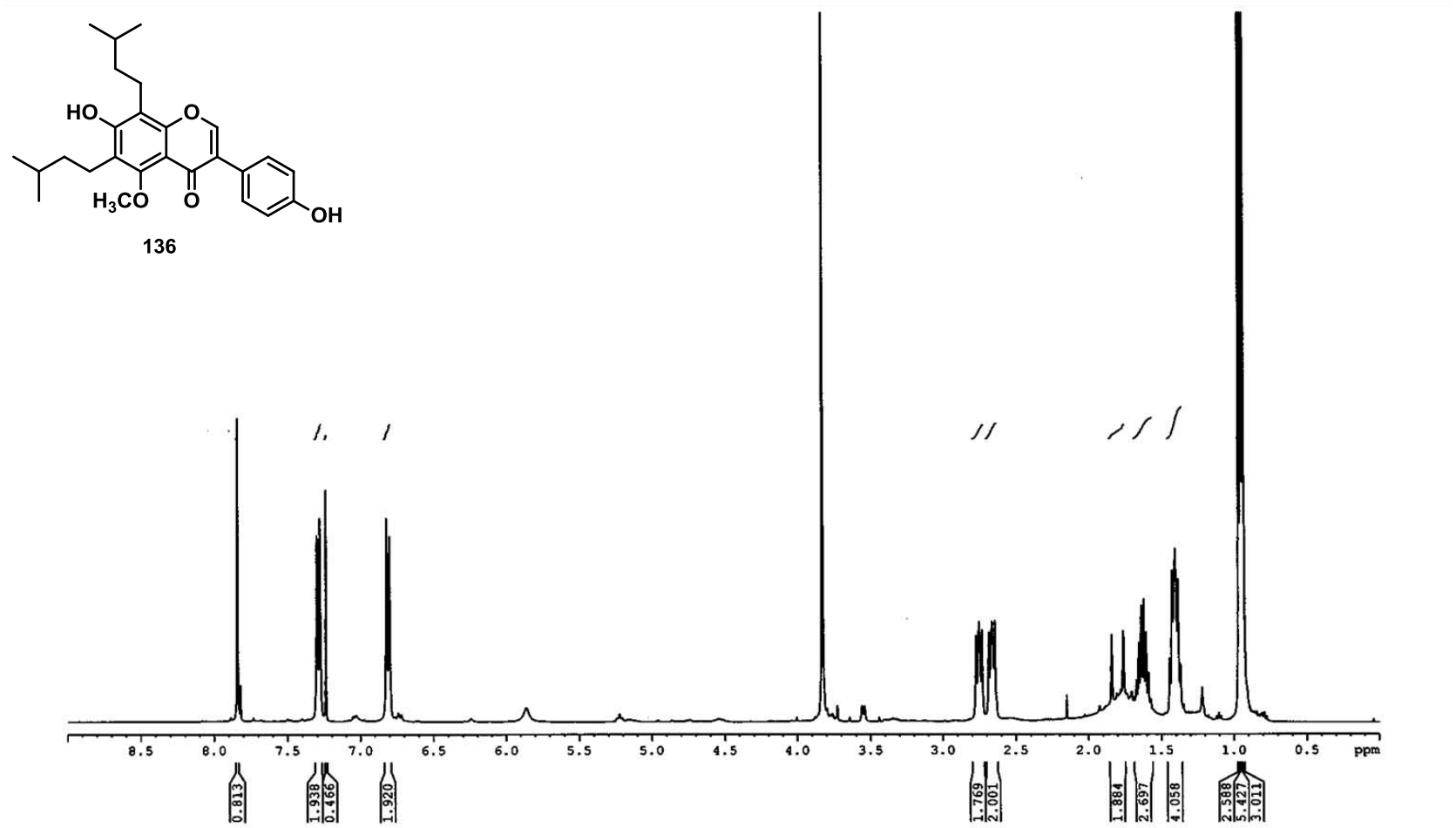


Figure 21 ^{1}H-NMR Spectrum of Tetrahydroderrisisoflavone A (**136**) in $CDCl_3$ + 2 Drops of CD_3OD

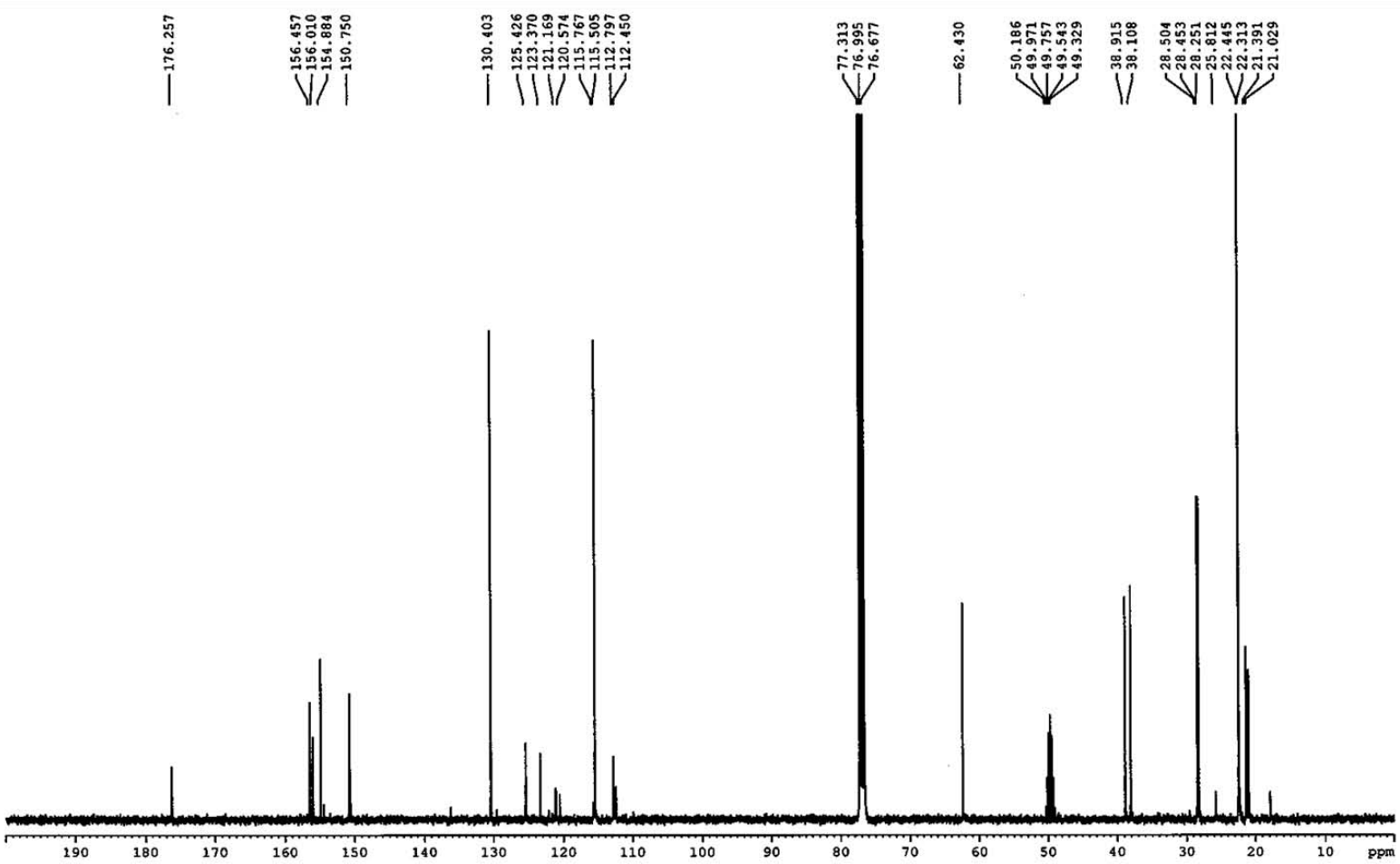


Figure 21a ^{13}C-NMR Spectrum of Tetrahydroderrisisoflavone A (**136**) in $CDCl_3$ + 2 Drops of CD_3OD

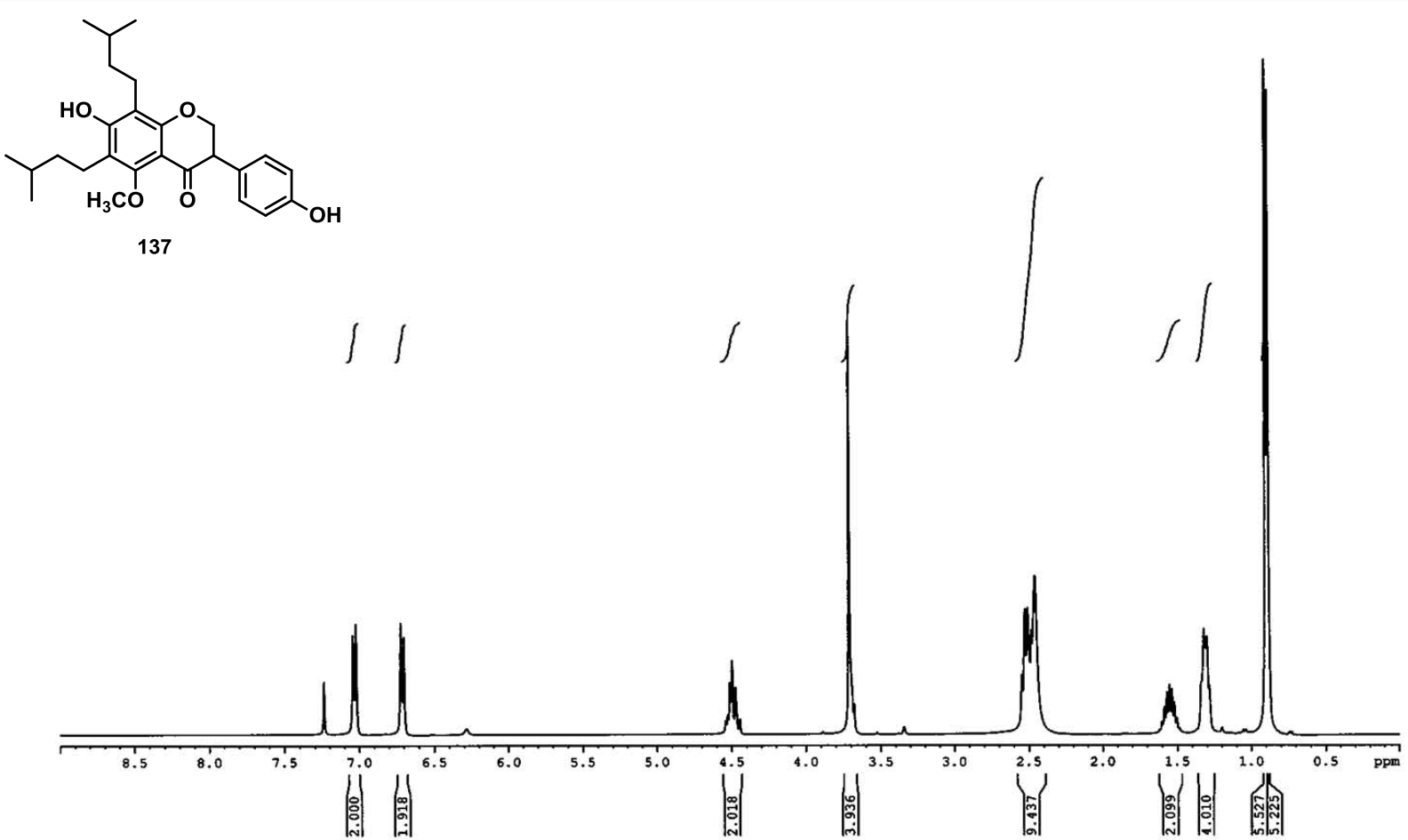


Figure 22 ^{1}H-NMR Spectrum of Hexahydroderrisisoflavone A (**137**) in $CDCl_3$ + 2 Drops of CD_3OD

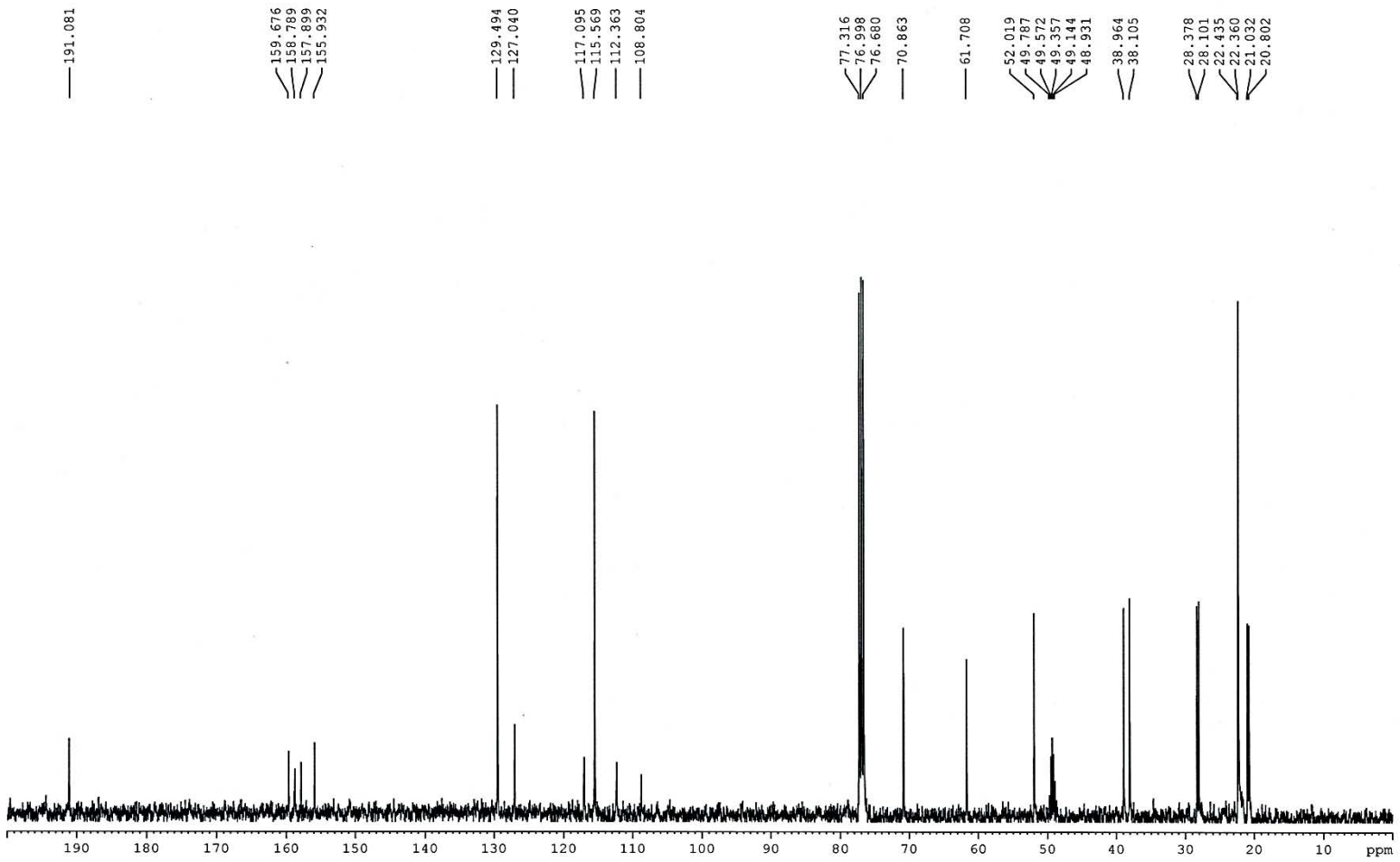


Figure 22a ^{13}C-NMR Spectrum of Hexahydroderrisisoflavone A (**137**) in $CDCl_3$ + 2 Drops of CD_3OD

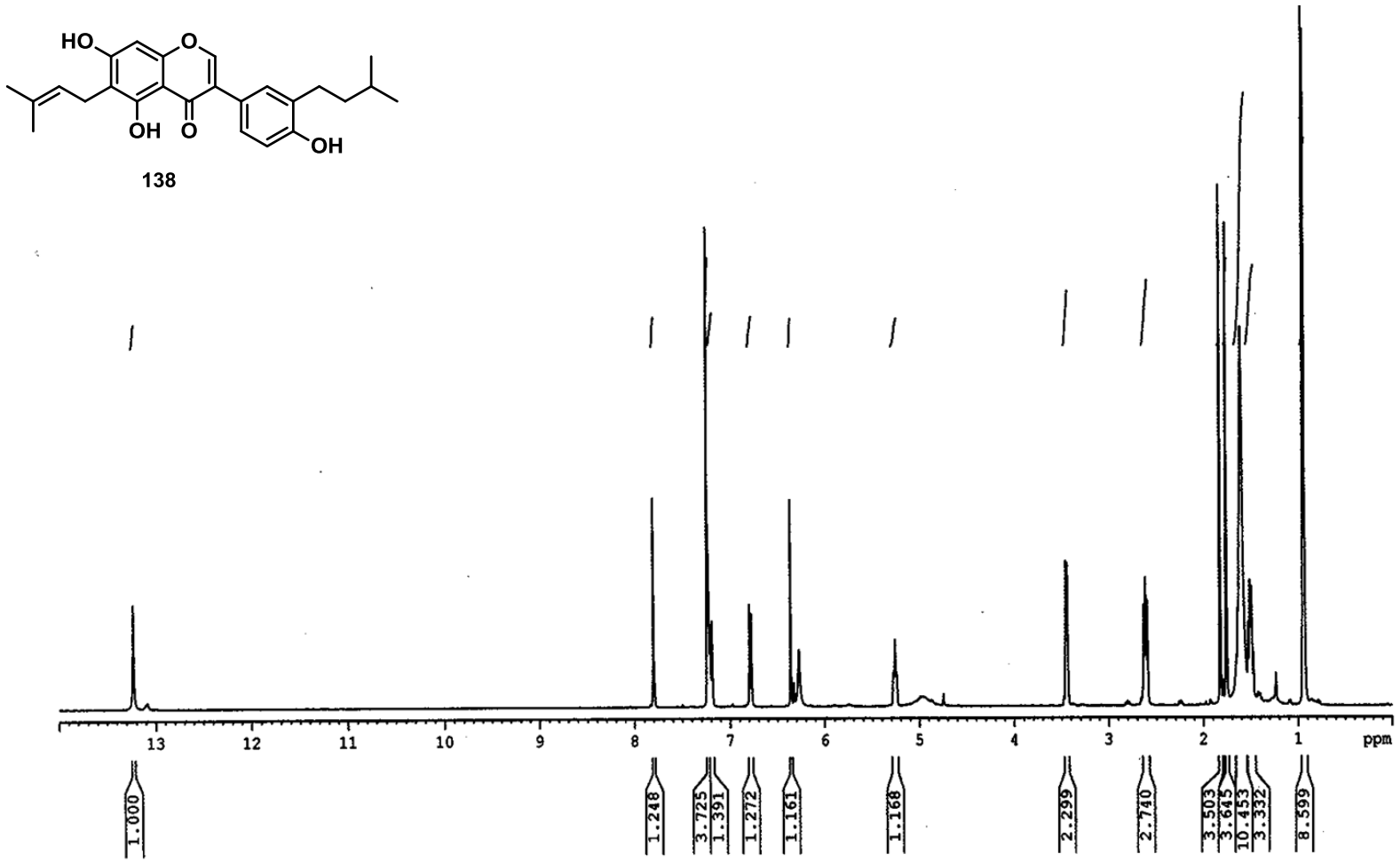


Figure 23 ^{1}H-NMR Spectrum of Dihydrolupalbigenin (**138**) in $CDCl_3$

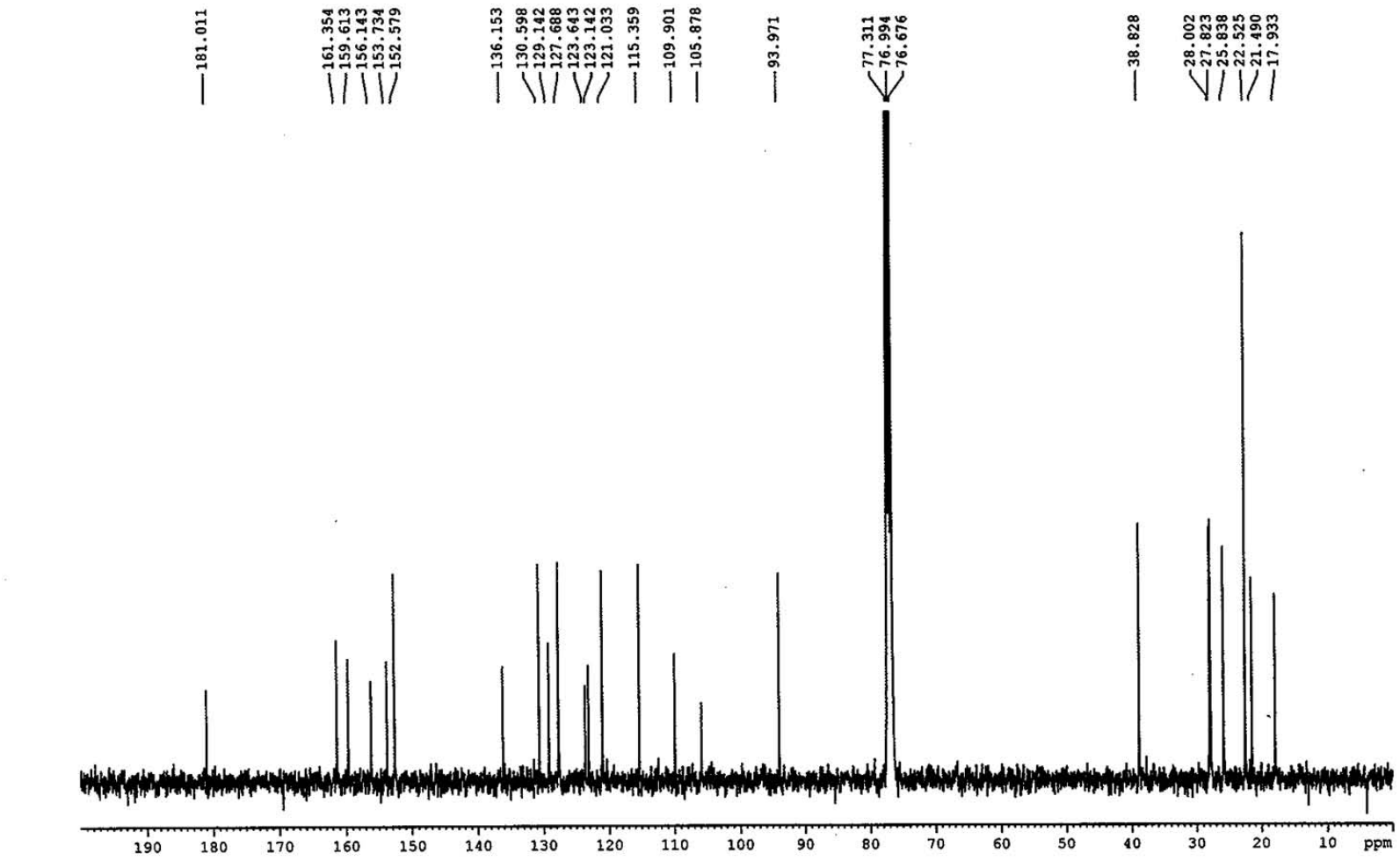


Figure 23a ^{13}C-NMR Spectrum of Dihydrolupalbigenin (**138**) in $CDCl_3$

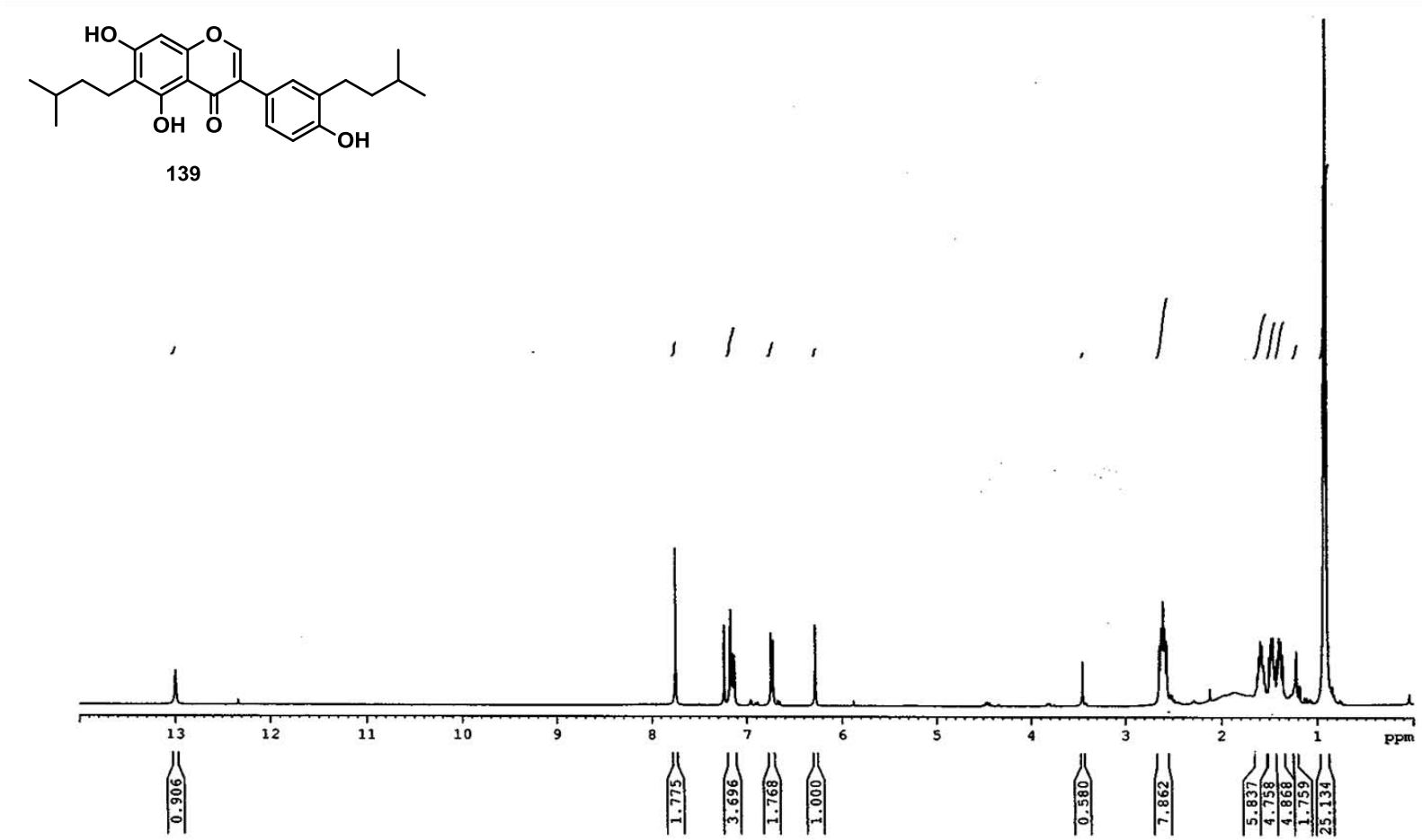


Figure 24 ^{1}H-NMR Spectrum of Tetrahydrolupalbigenin (**139**) in CD_3OD + $CDCl_3$

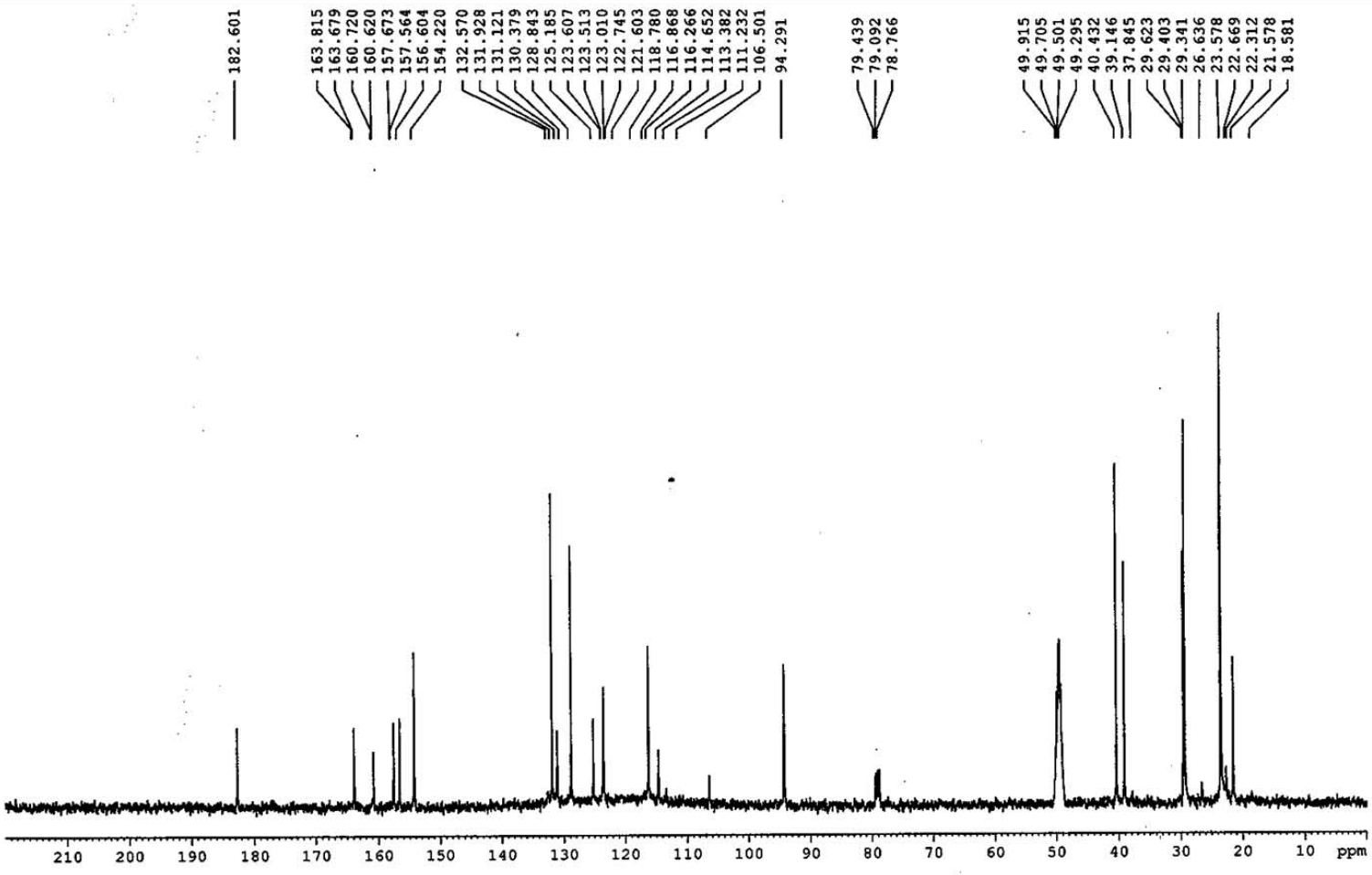


Figure 24a ^{13}C-NMR Spectrum of Tetrahydrolupalbigenin (**139**) in CD_3OD + $CDCl_3$

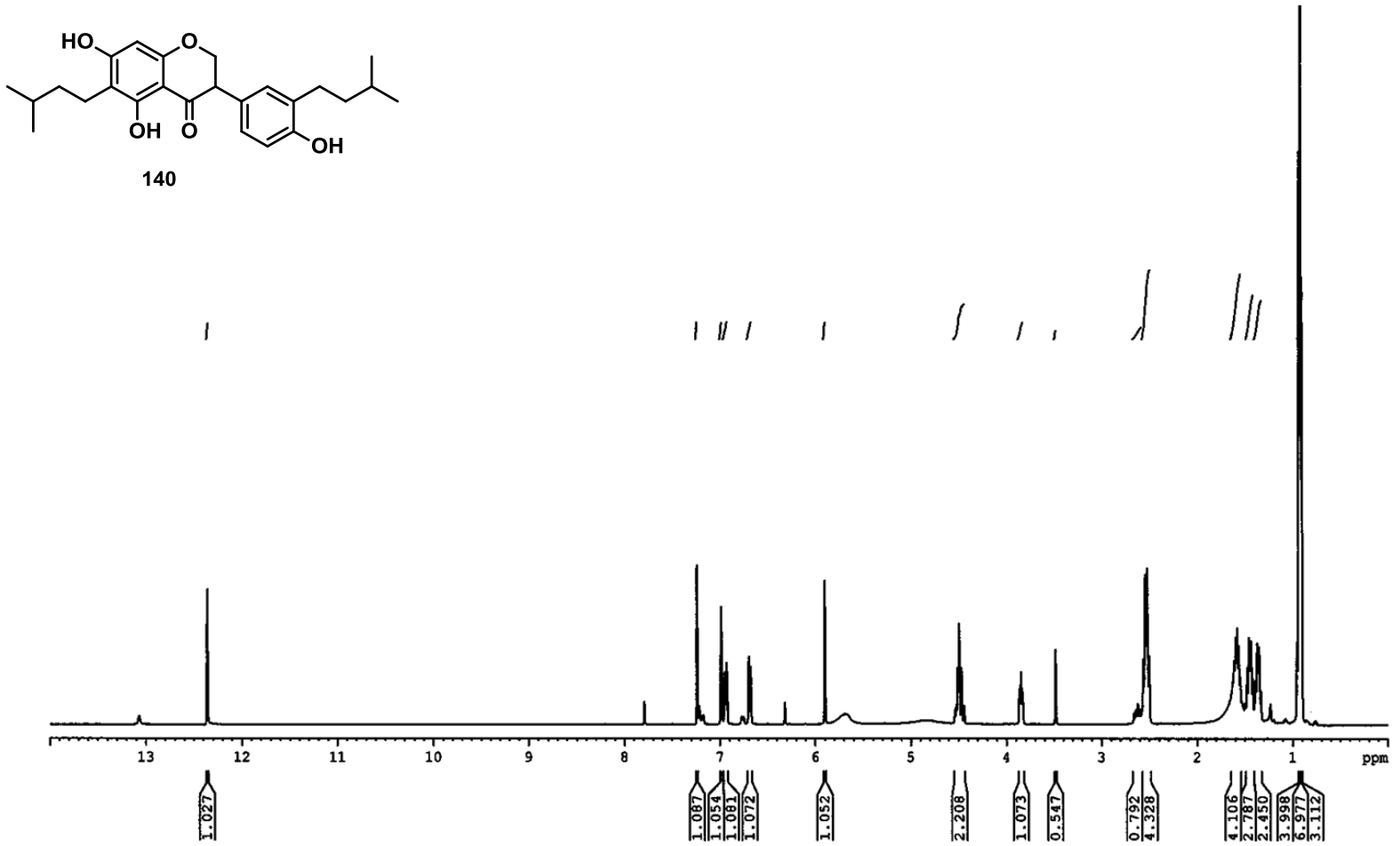


Figure 25 ^{1}H-NMR Spectrum of Hexahydrolupalbigenin (**140**) in $CDCl_3$

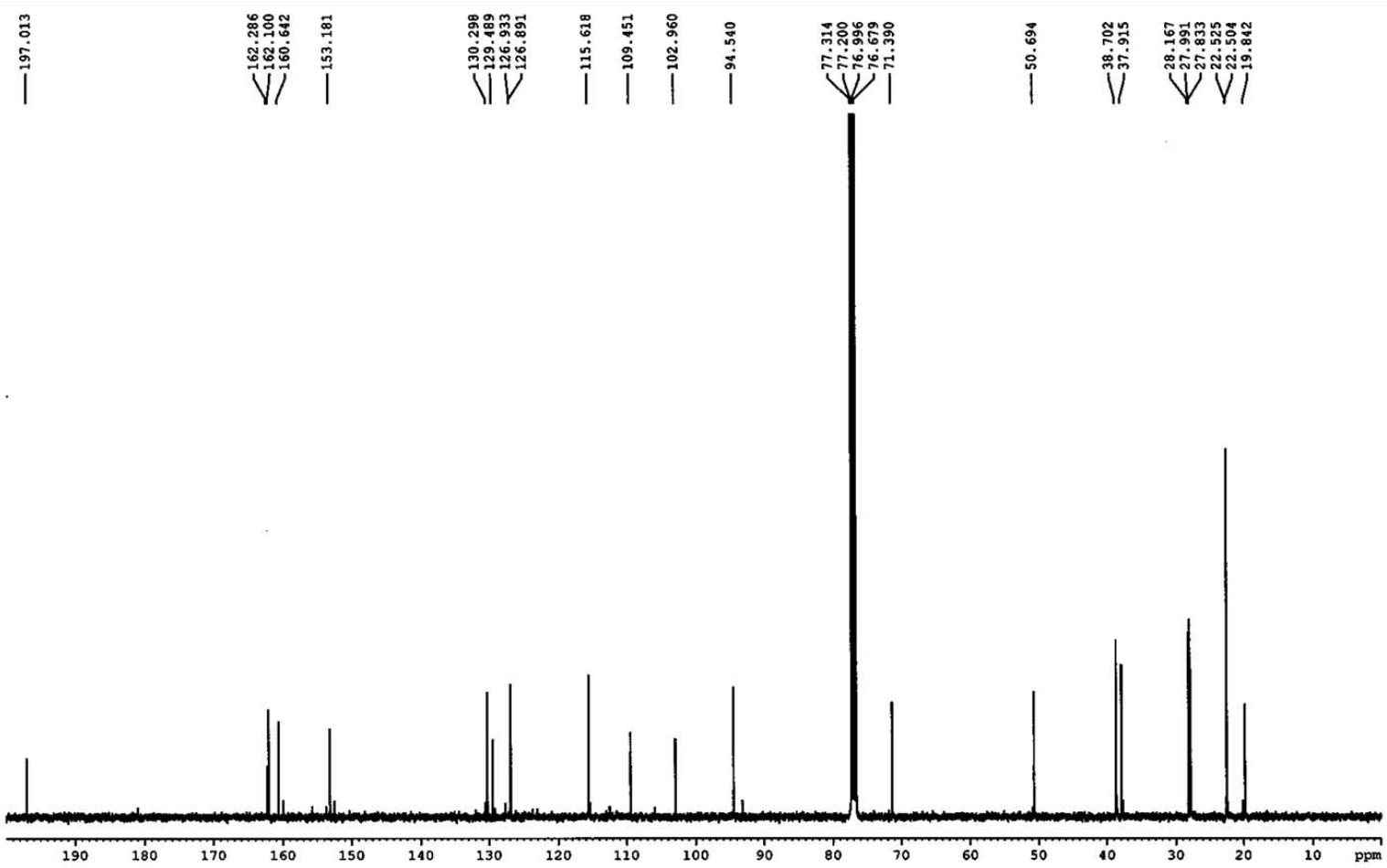


Figure 25a ^{13}C-NMR Spectrum of Hexahydrolupalbigenin (**140**) in $CDCl_3$

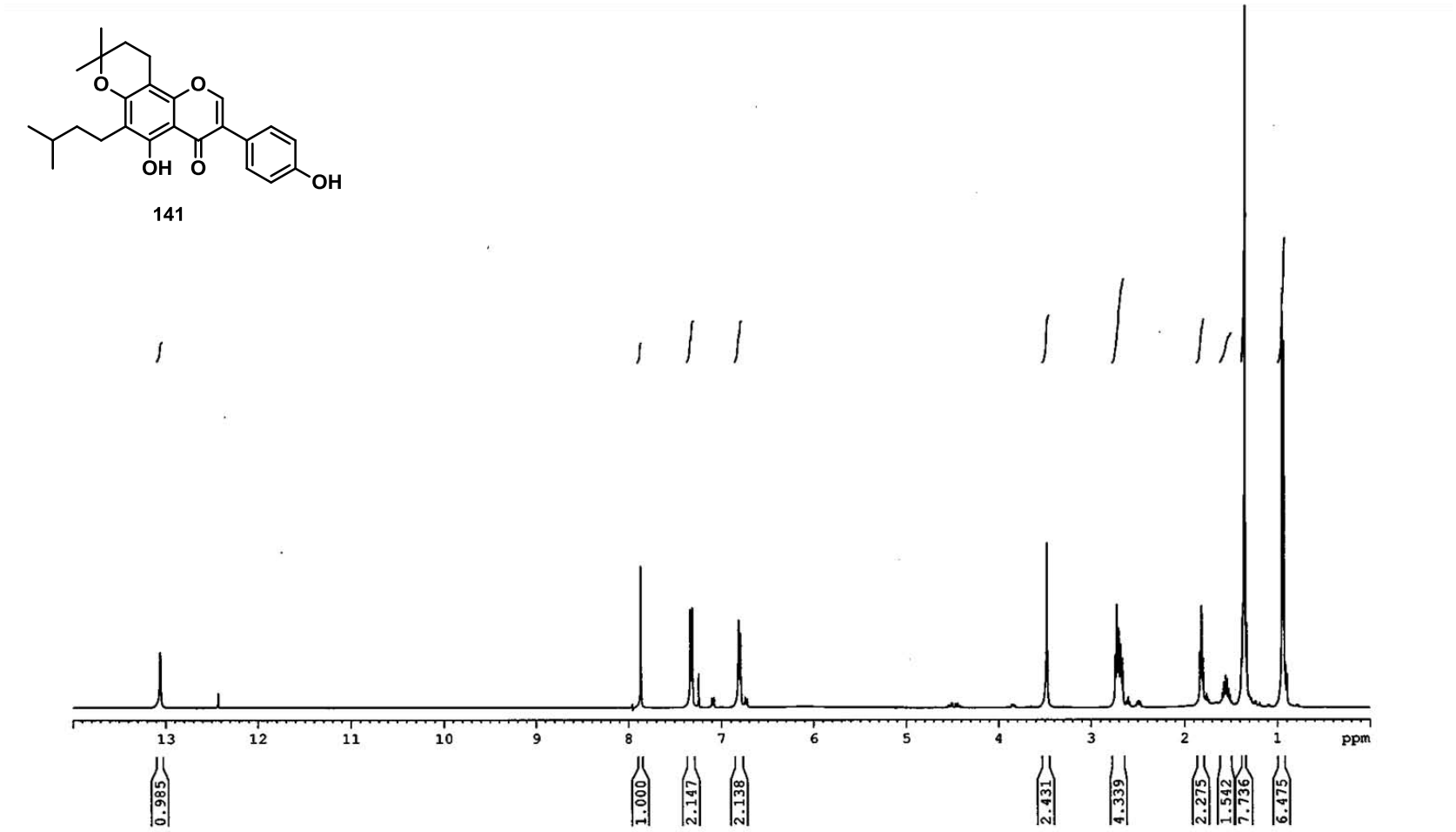


Figure 26 ^{1}H-NMR Spectrum of Tetrahydroosajin (**141**) in $CDCl_3$

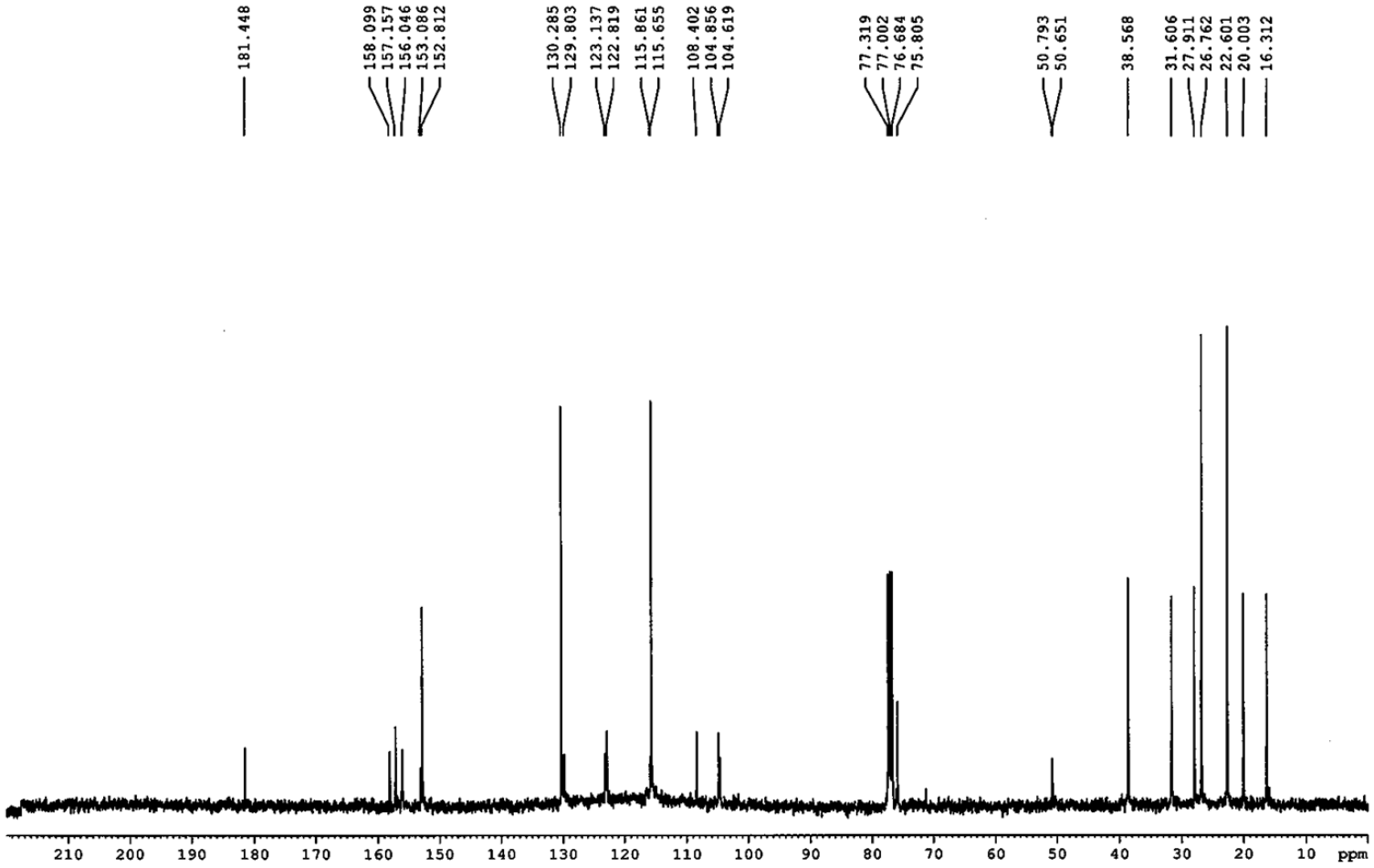


Figure 26a ^{13}C-NMR Spectrum of Tetrahydroosajin (**141**) in $CDCl_3$

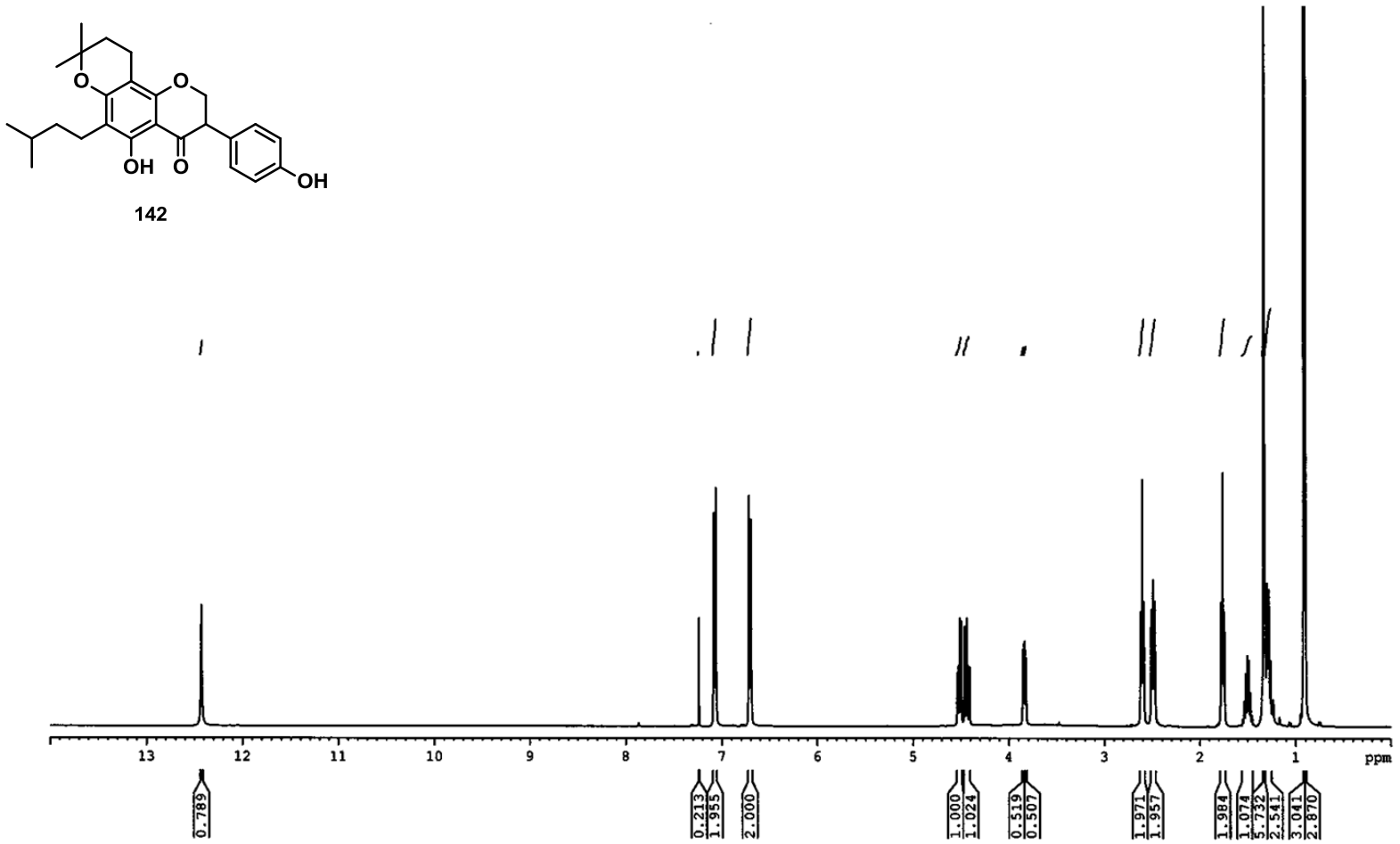


Figure 27 ^{1}H-NMR Spectrum of Hexahydroosajin (**142**) in $CDCl_3$

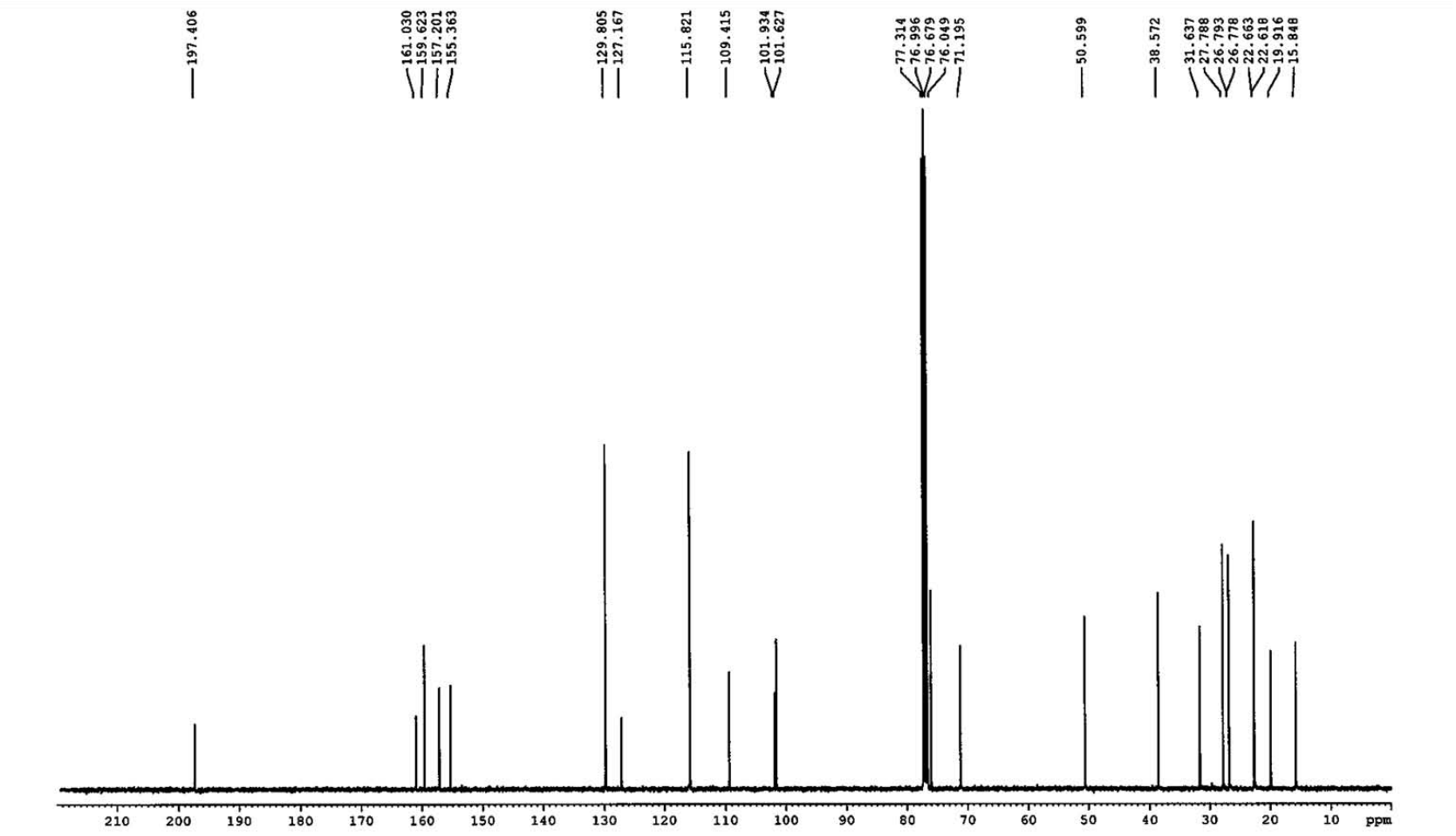


Figure 27a ^{13}C-NMR Spectrum of Hexahydroosajin (**142**) in $CDCl_3$

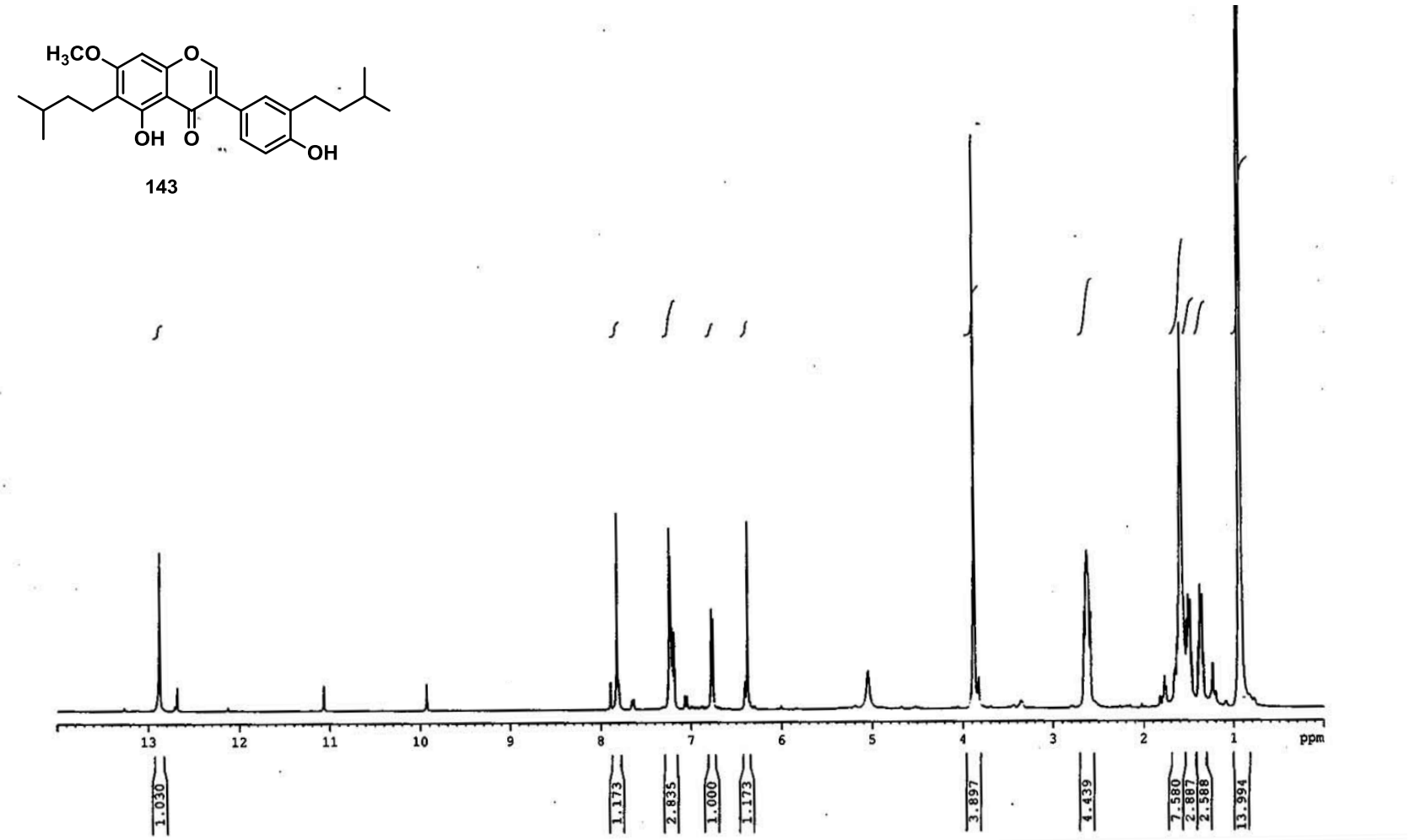


Figure 28 ^{1}H-NMR Spectrum of Tetrahydrolupalbigenin 7-*O*-methyl ether (**143**) in $CDCl_3$

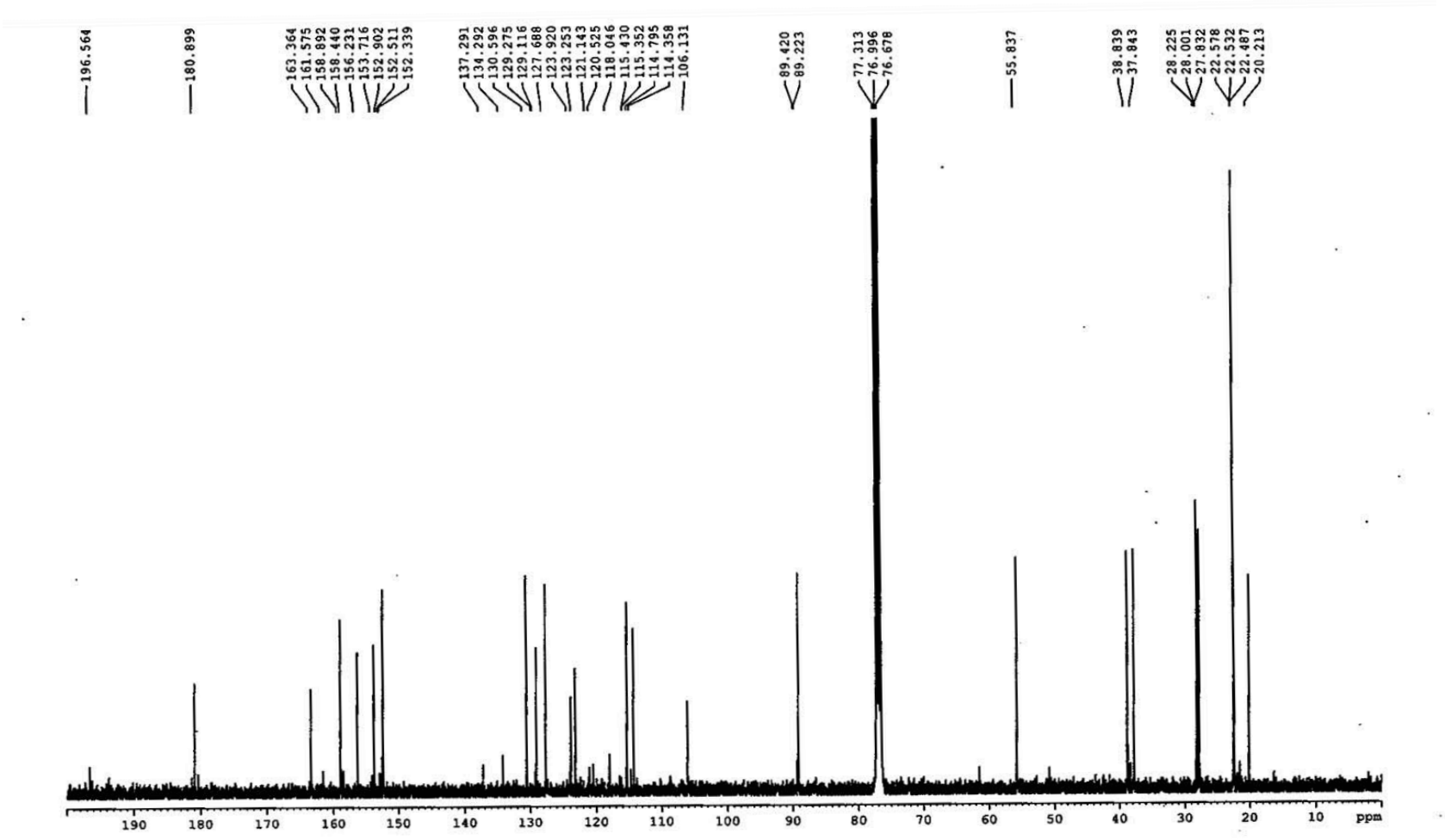


Figure 28a ^{13}C-NMR Spectrum of Tetrahydrolupalbigenin 7-*O*-methyl ether (**143**) in $CDCl_3$

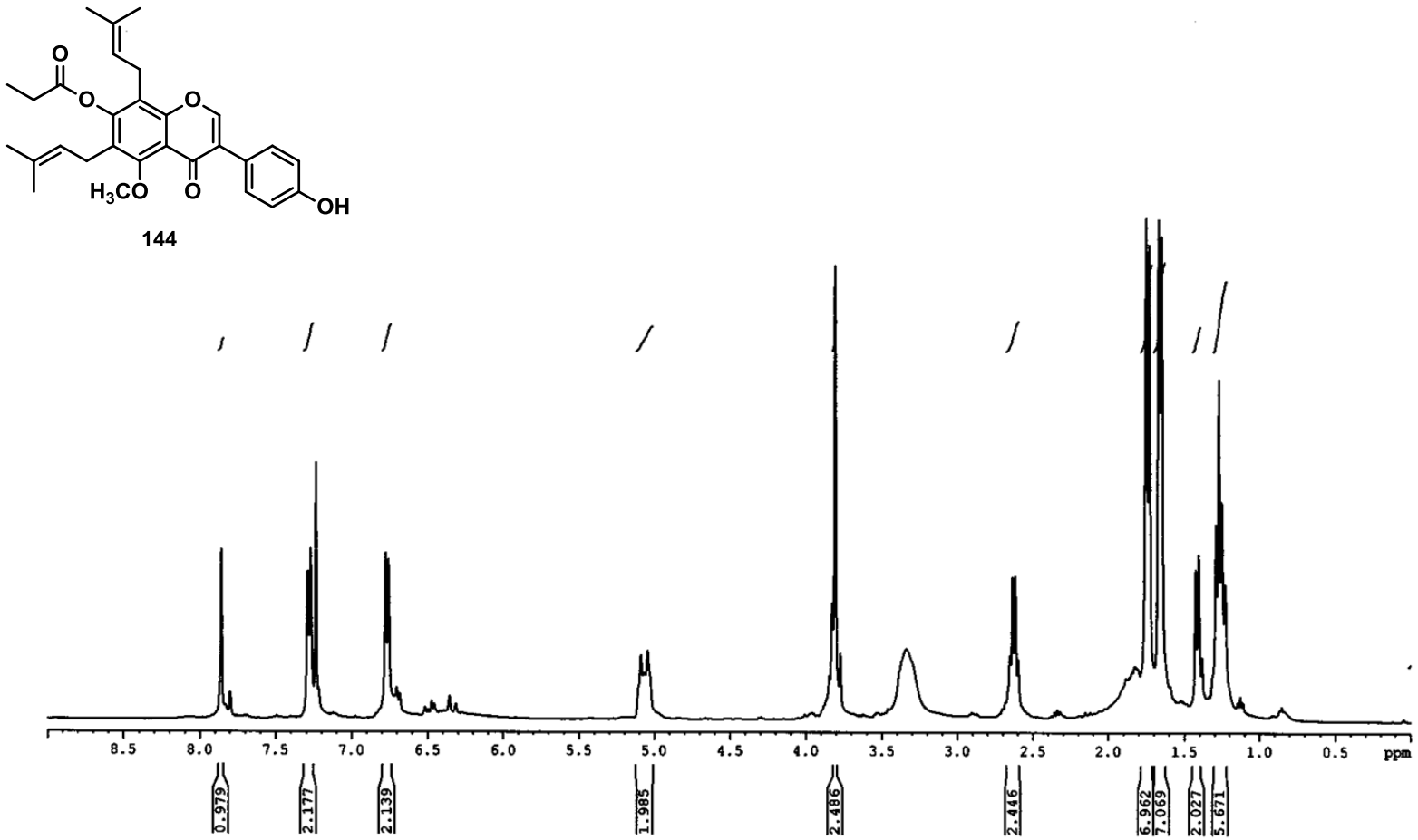


Figure 29 ^{1}H-NMR Spectrum of Derrisisoflavone A 7-*O*-propanoate (**144**) in $CDCl_3$

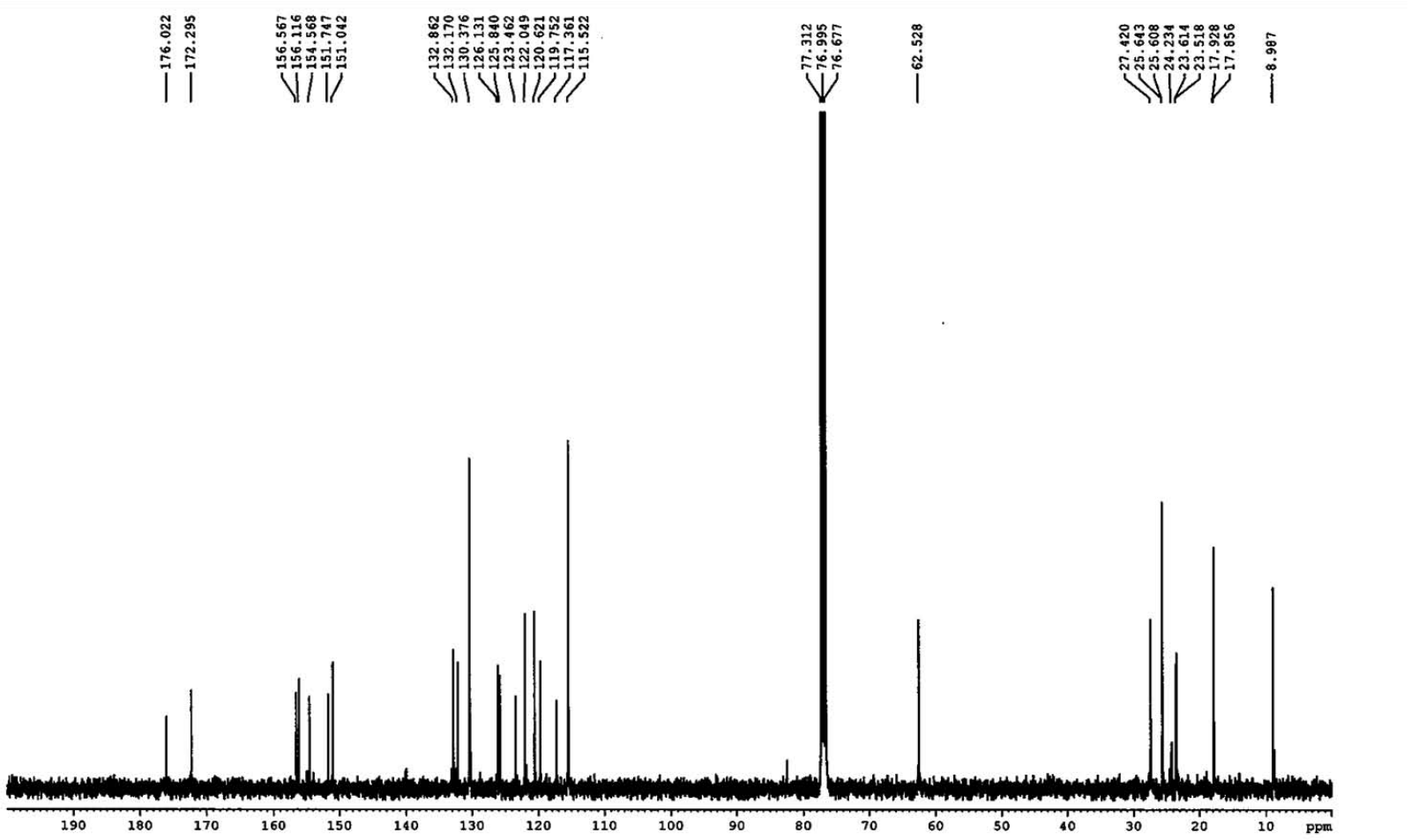


Figure 29a ^{13}C-NMR Spectrum of Derrisisoflavone A 7-*O*-propanoate (**144**) in $CDCl_3$

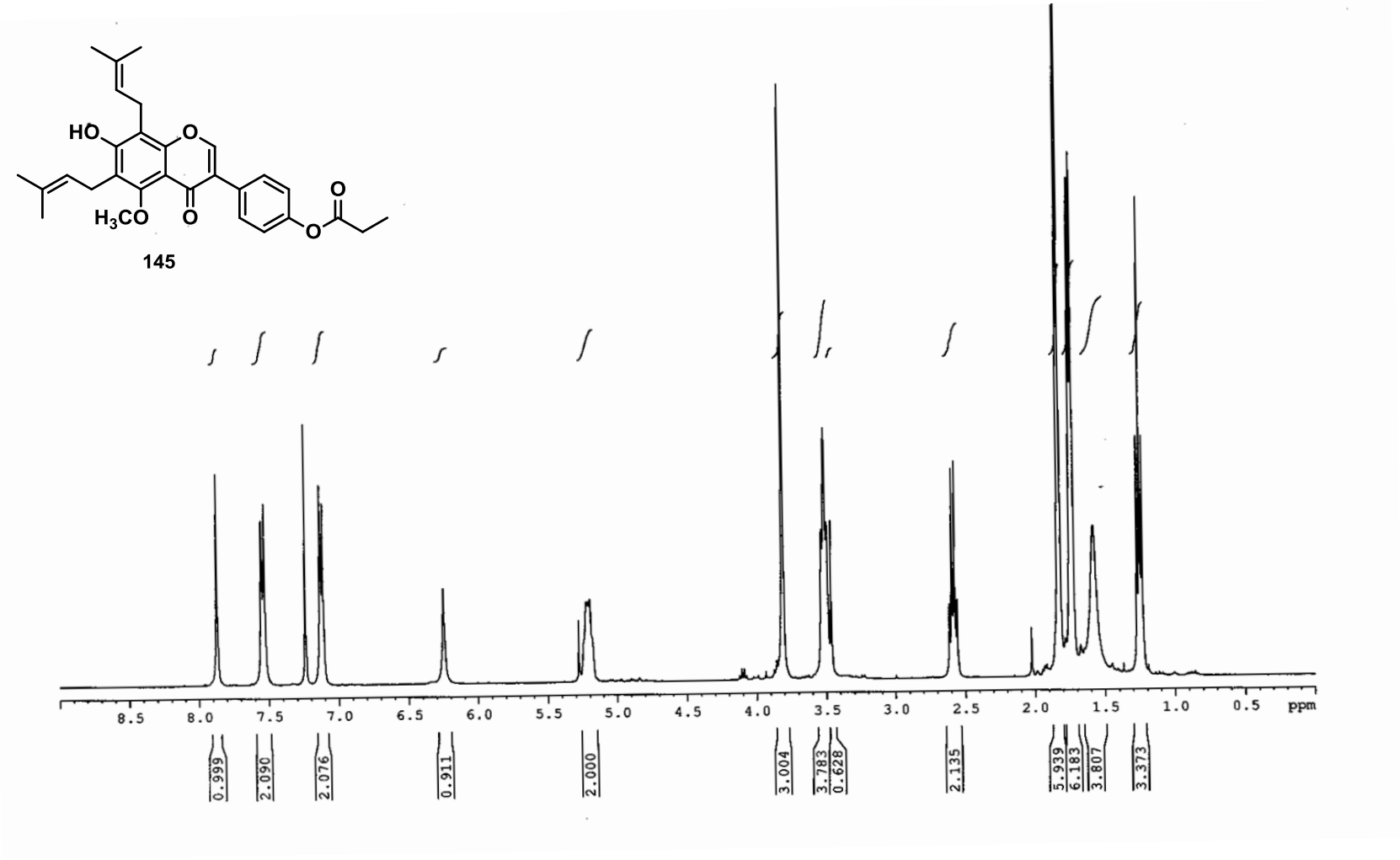


Figure 30 ^{1}H-NMR Spectrum of Derrisisoflavone A 4′-*O*-propanoate (**145**) in $CDCl_3$

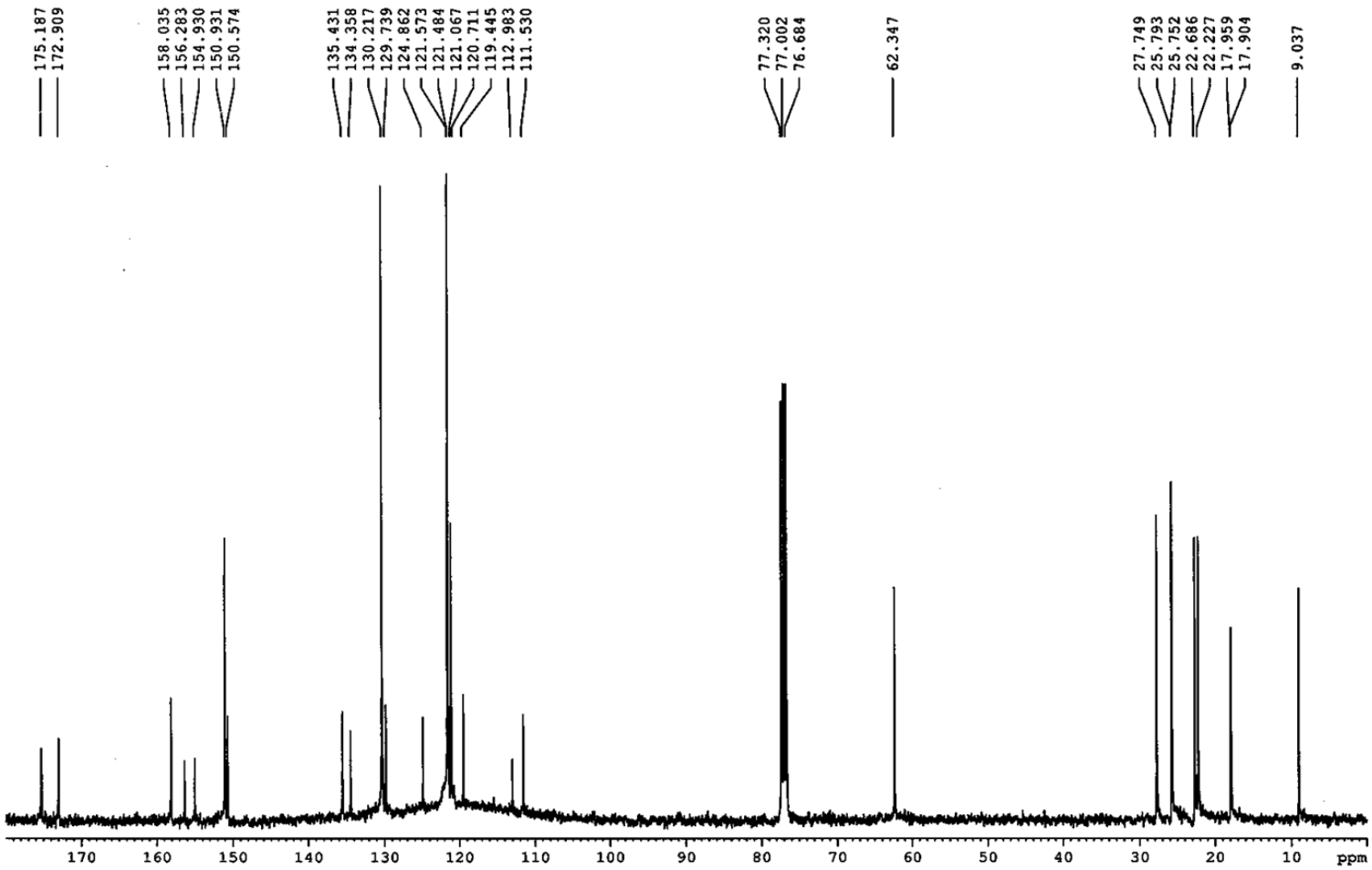


Figure 30a ^{13}C-NMR Spectrum of Derrisisoflavone A 4′-*O*-propanoate (**145**) in $CDCl_3$

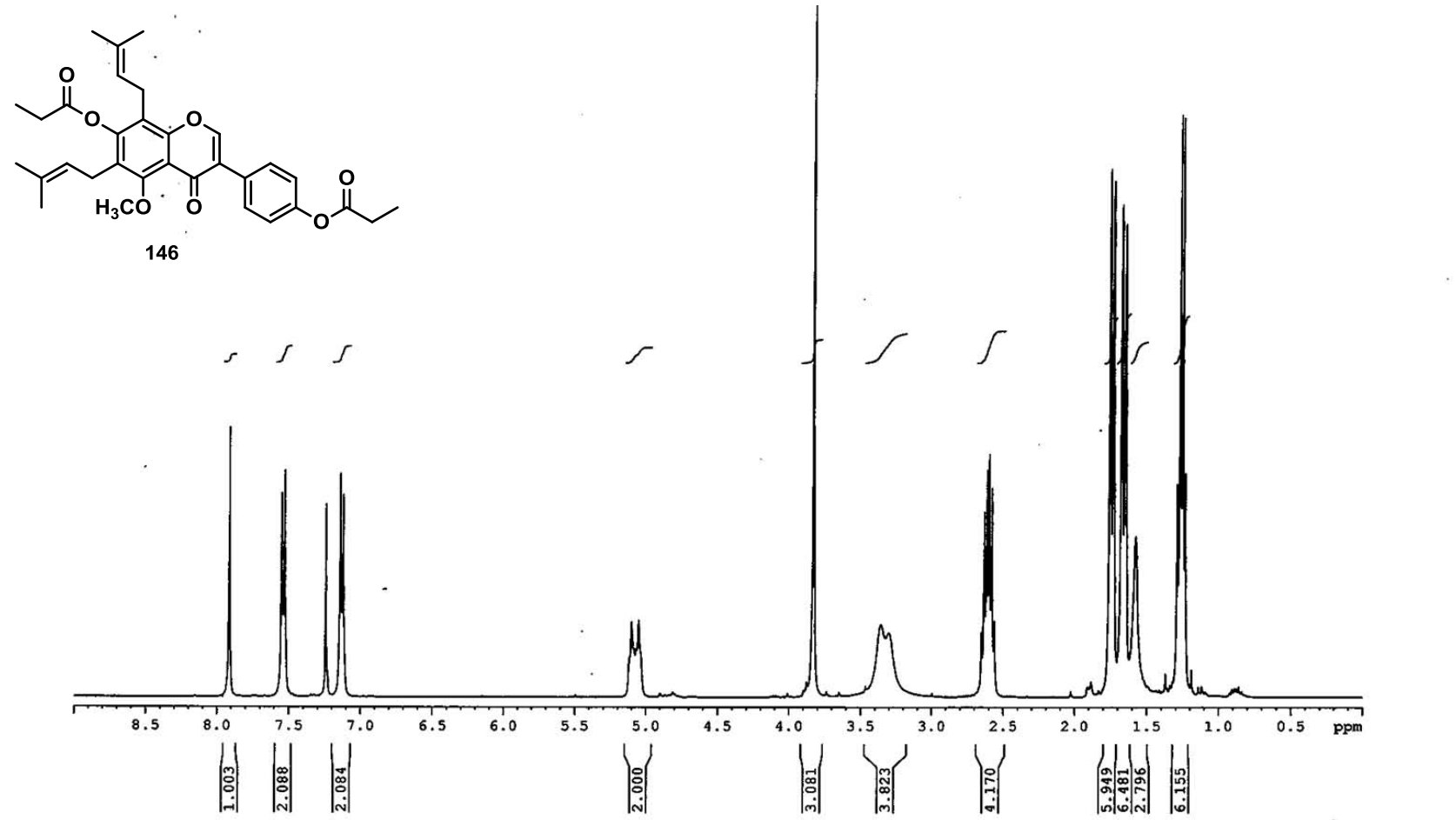


Figure 31 ^{1}H-NMR Spectrum of Derrisisoflavone A 7,4′-di-*O*-propanoate (**146**) in $CDCl_3$

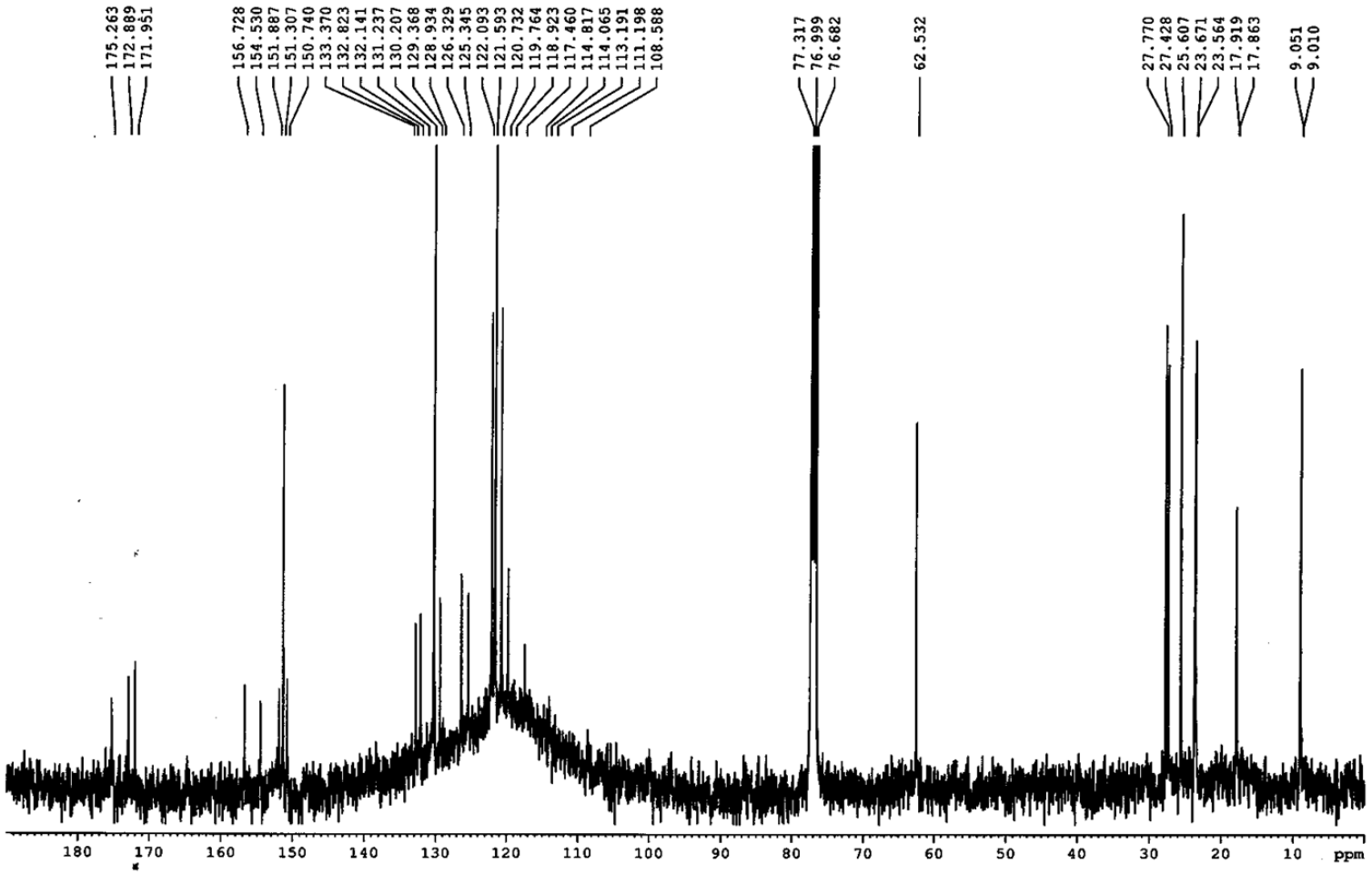


Figure 31a ^{13}C-NMR Spectrum of Derrisisoflavone A 7,4′-di-*O*-propanoate (**146**) in $CDCl_3$

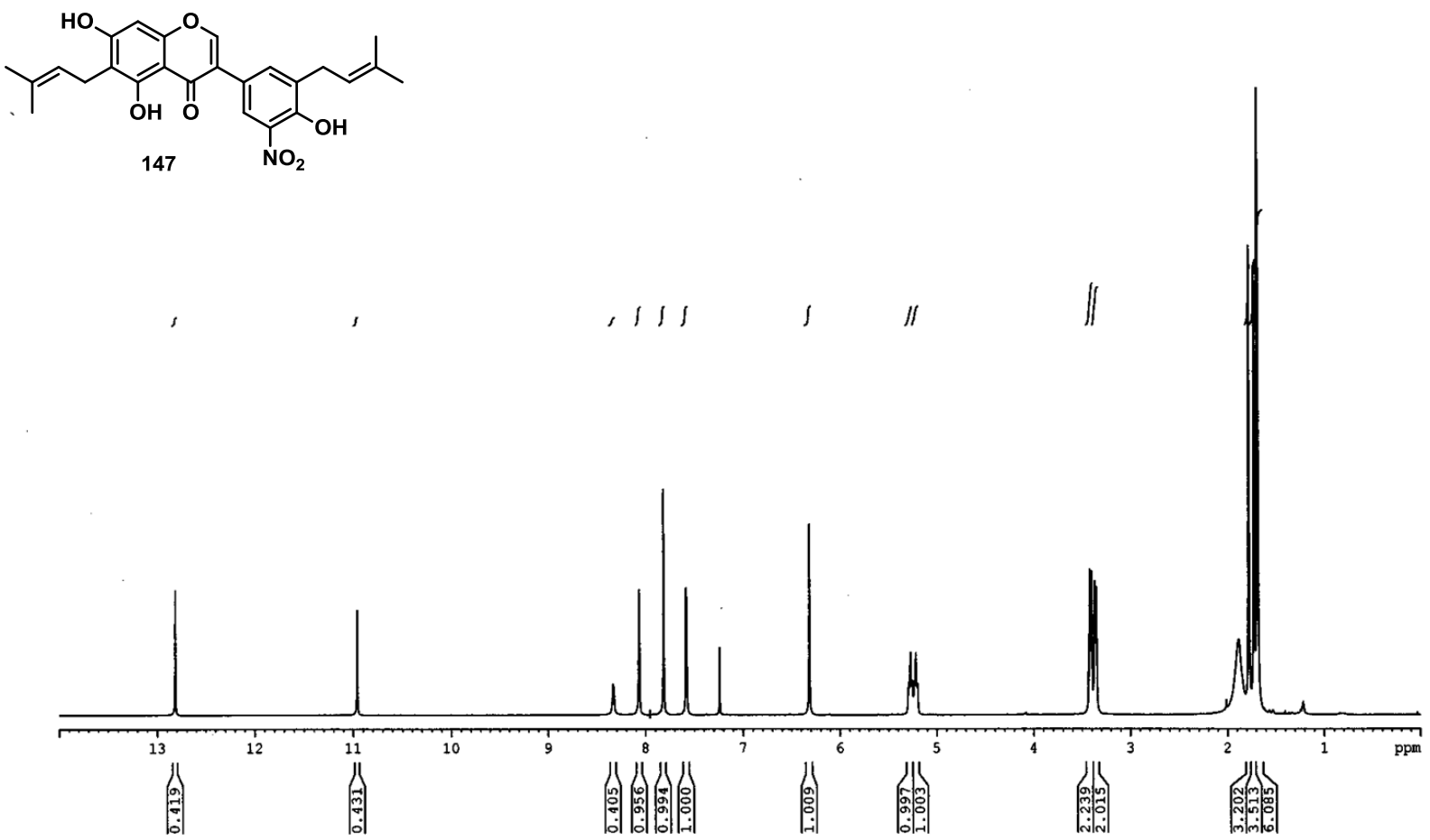


Figure 32 ^{1}H-NMR Spectrum of 5′-Nitrolupalbigenin (**147**) in $CDCl_3$ + 2 Drops of CD_3OD

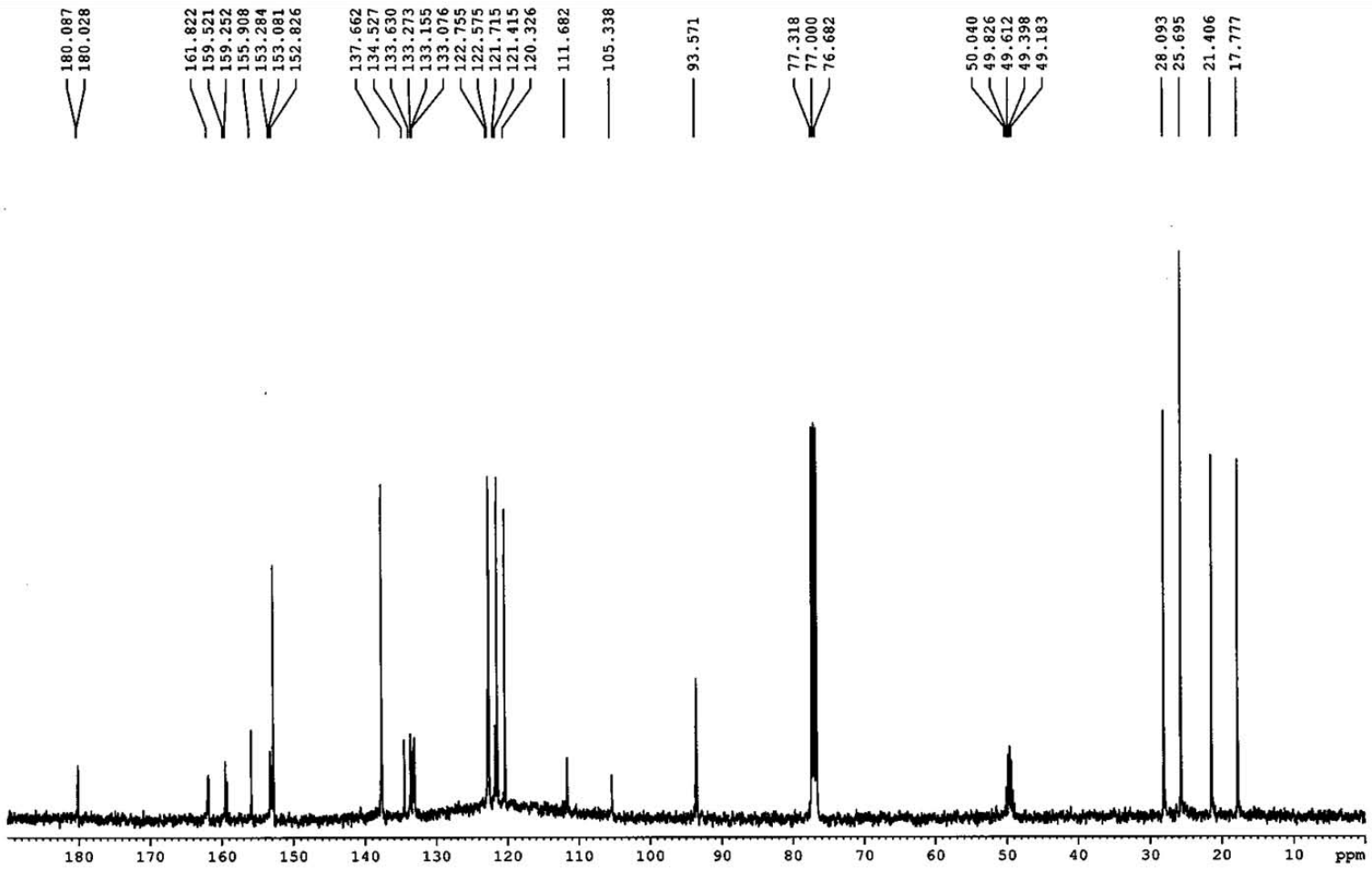


Figure 32a ^{13}C-NMR Spectrum of 5′-Nitrolupalbigenin (**147**) in $CDCl_3$ + 2 Drops of CD_3OD

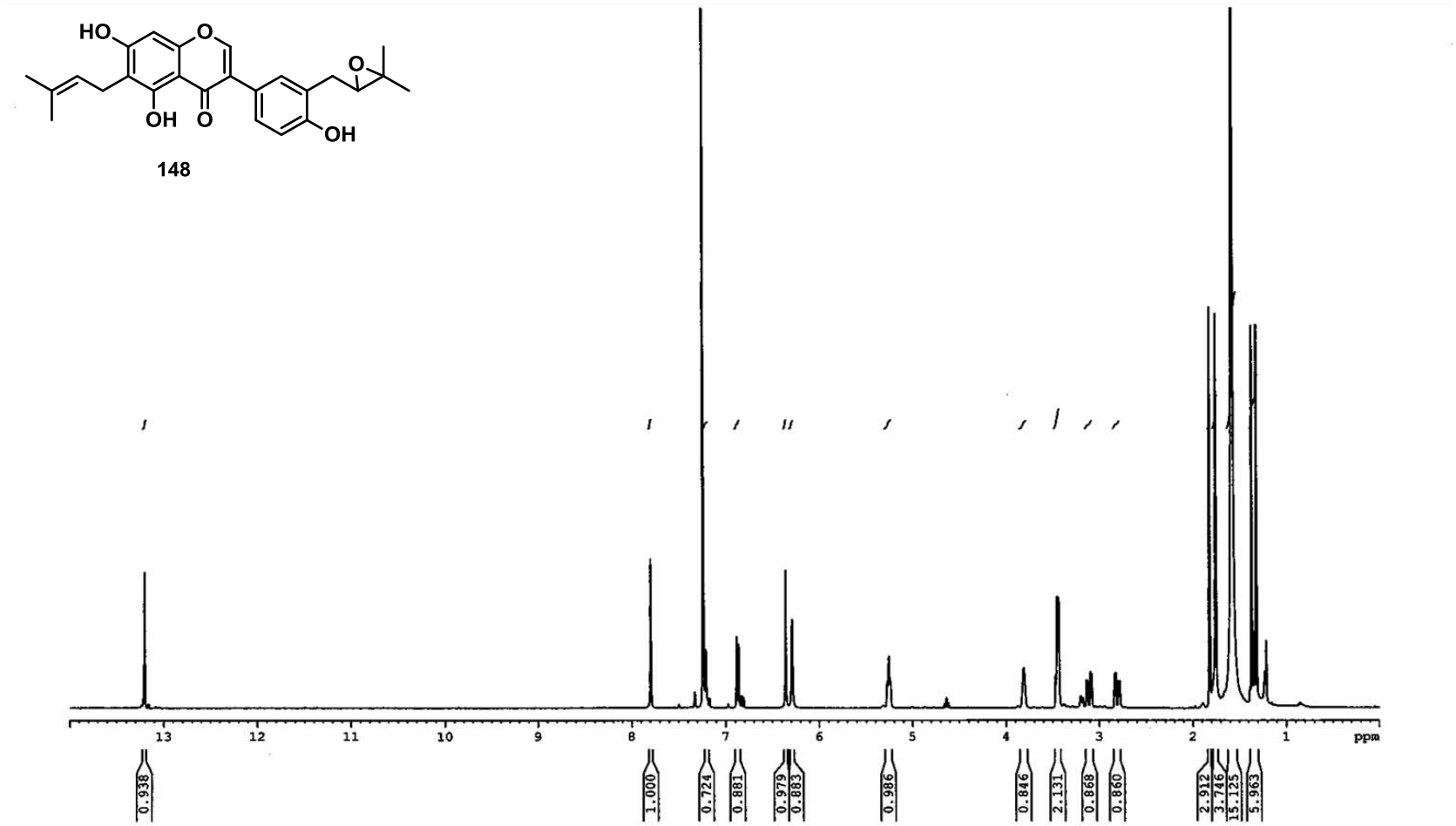


Figure 33 ^{1}H-NMR Spectrum of 2‴,3‴-Epoxylupalbigenin (**148**) in $CDCl_3$

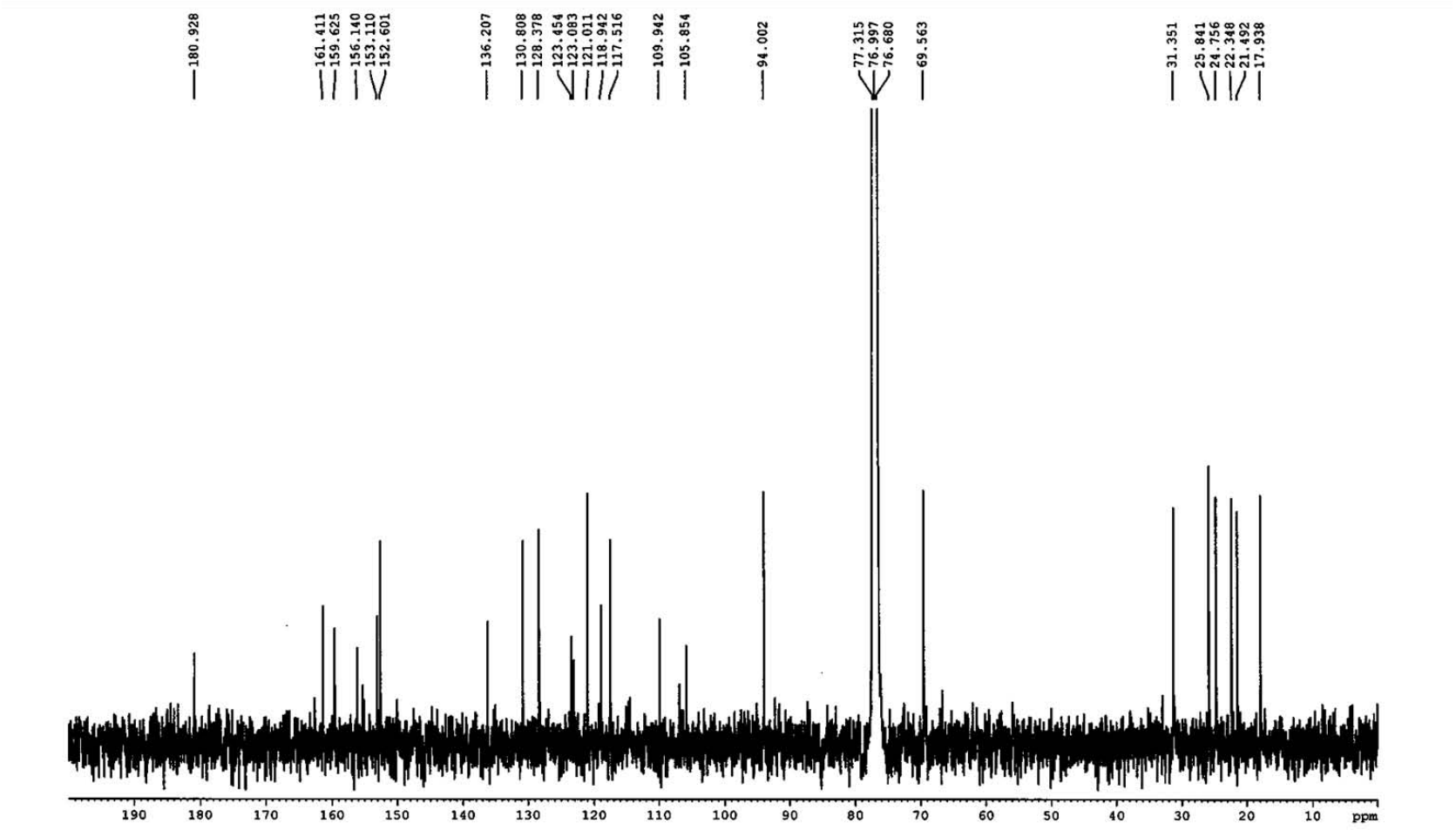


Figure 33a ^{13}C-NMR Spectrum of 2‴,3‴-Epoxylupalbigenin (**148**) in $CDCl_3$

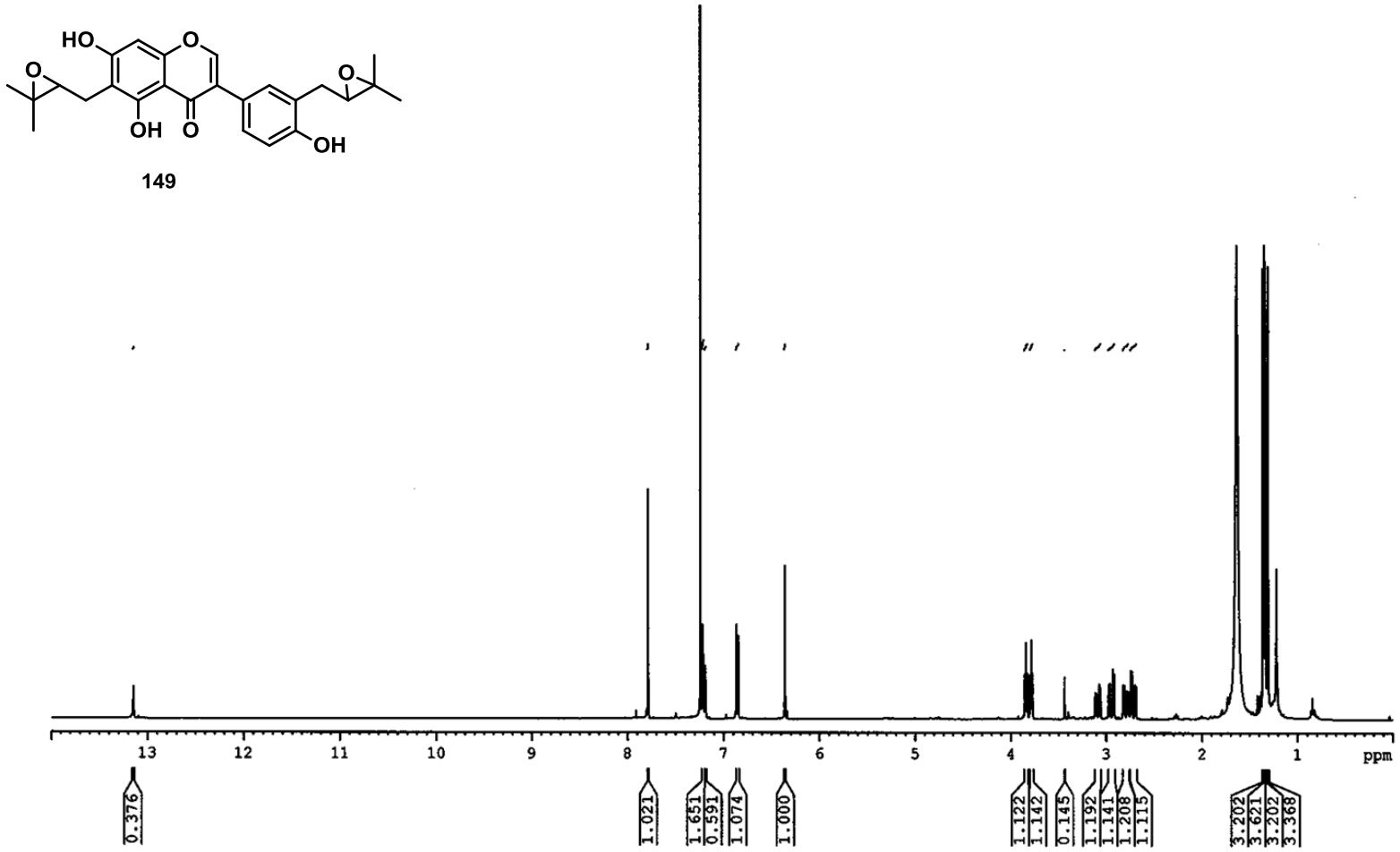


Figure 34 ^{1}H-NMR Spectrum of 2″,3″,2‴,3‴-Diepoxylupalbigenin (**149**) in CD_3OD

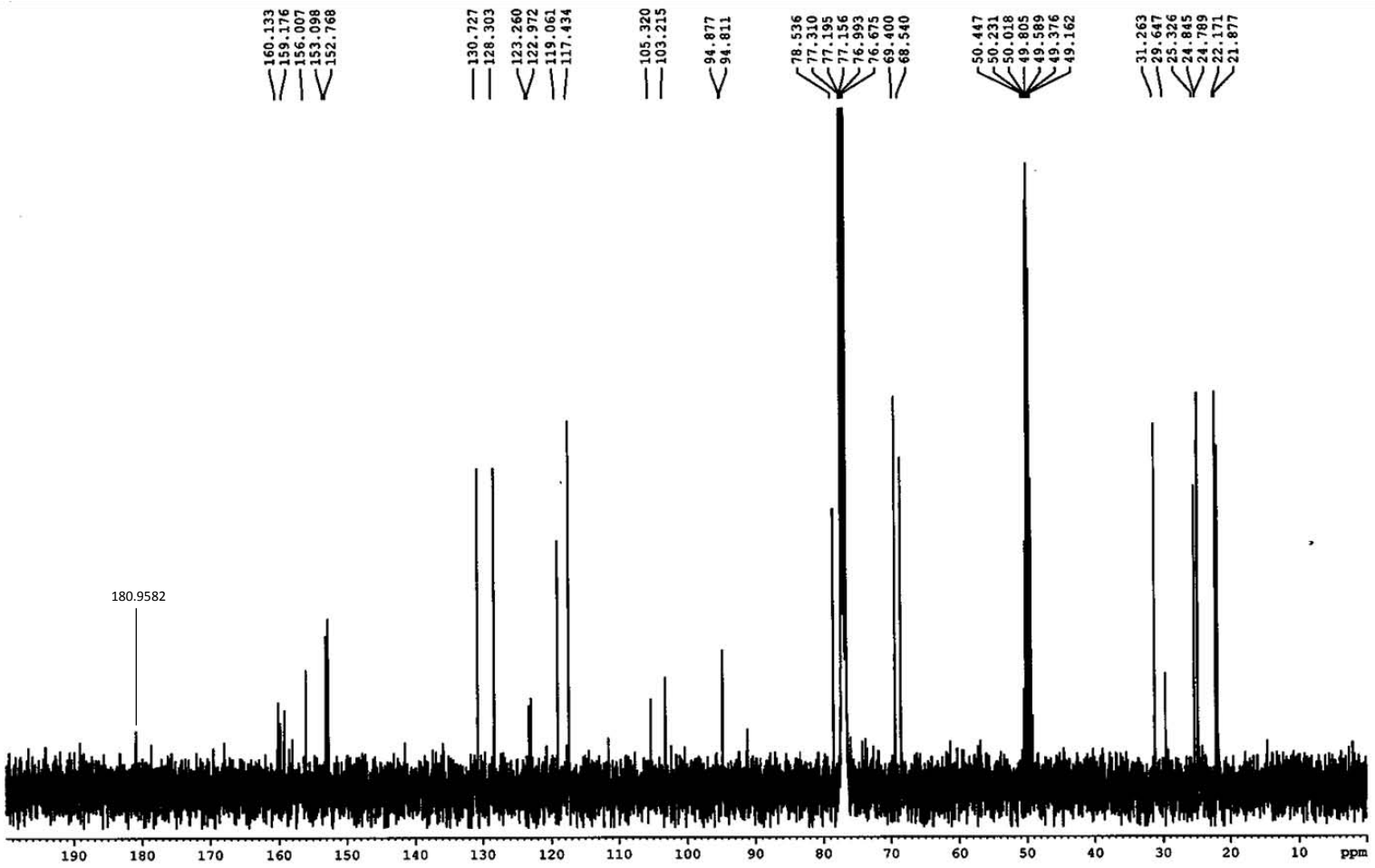


Figure 34a ^{13}C-NMR Spectrum of 2″,3″,2‴,3‴-Diepoxylupalbigenin (**149**) in CD_3OD

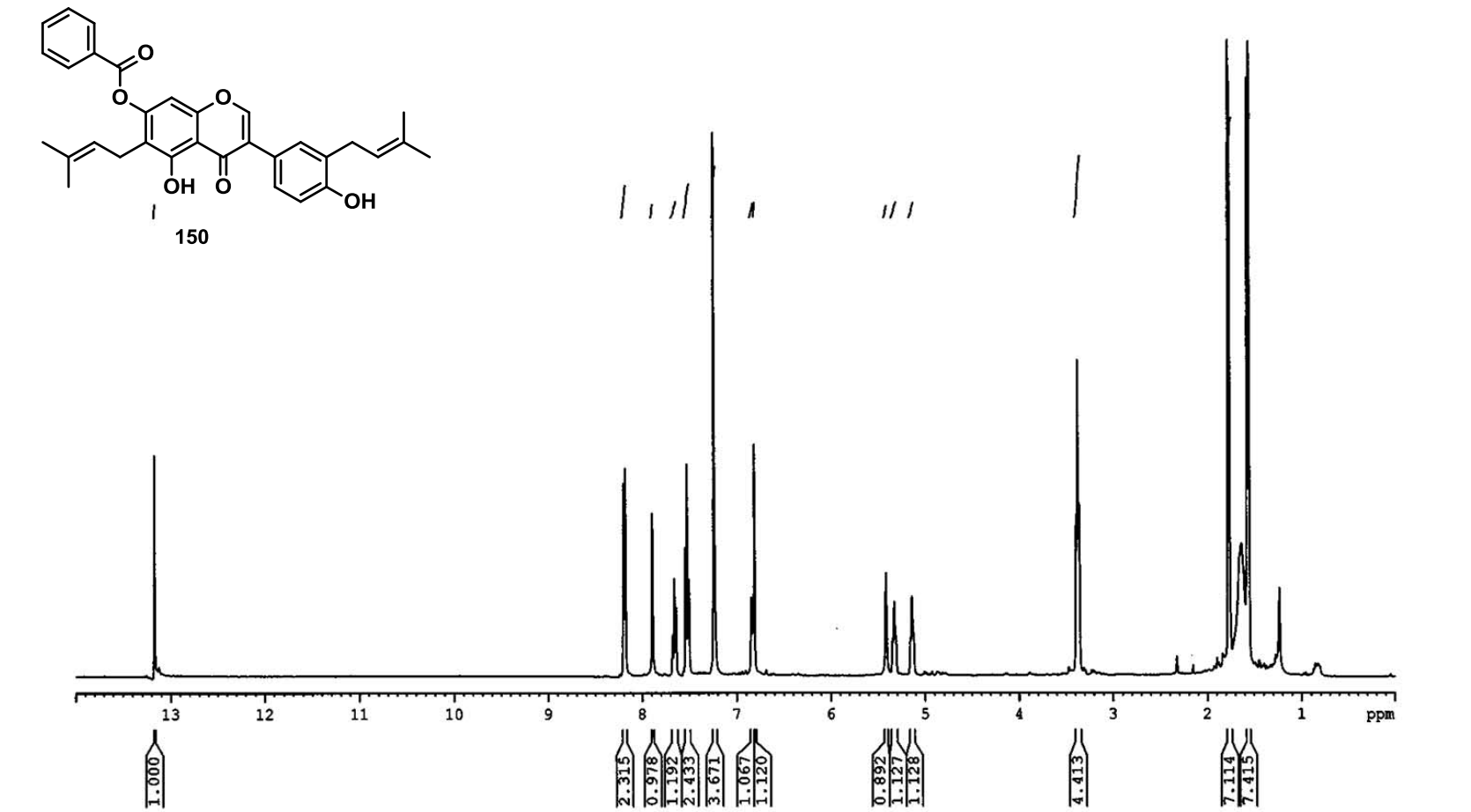


Figure 35 ^{1}H-NMR Spectrum of Lupalbigenin 7-*O*-benzoate (**150**) in $CDCl_3$

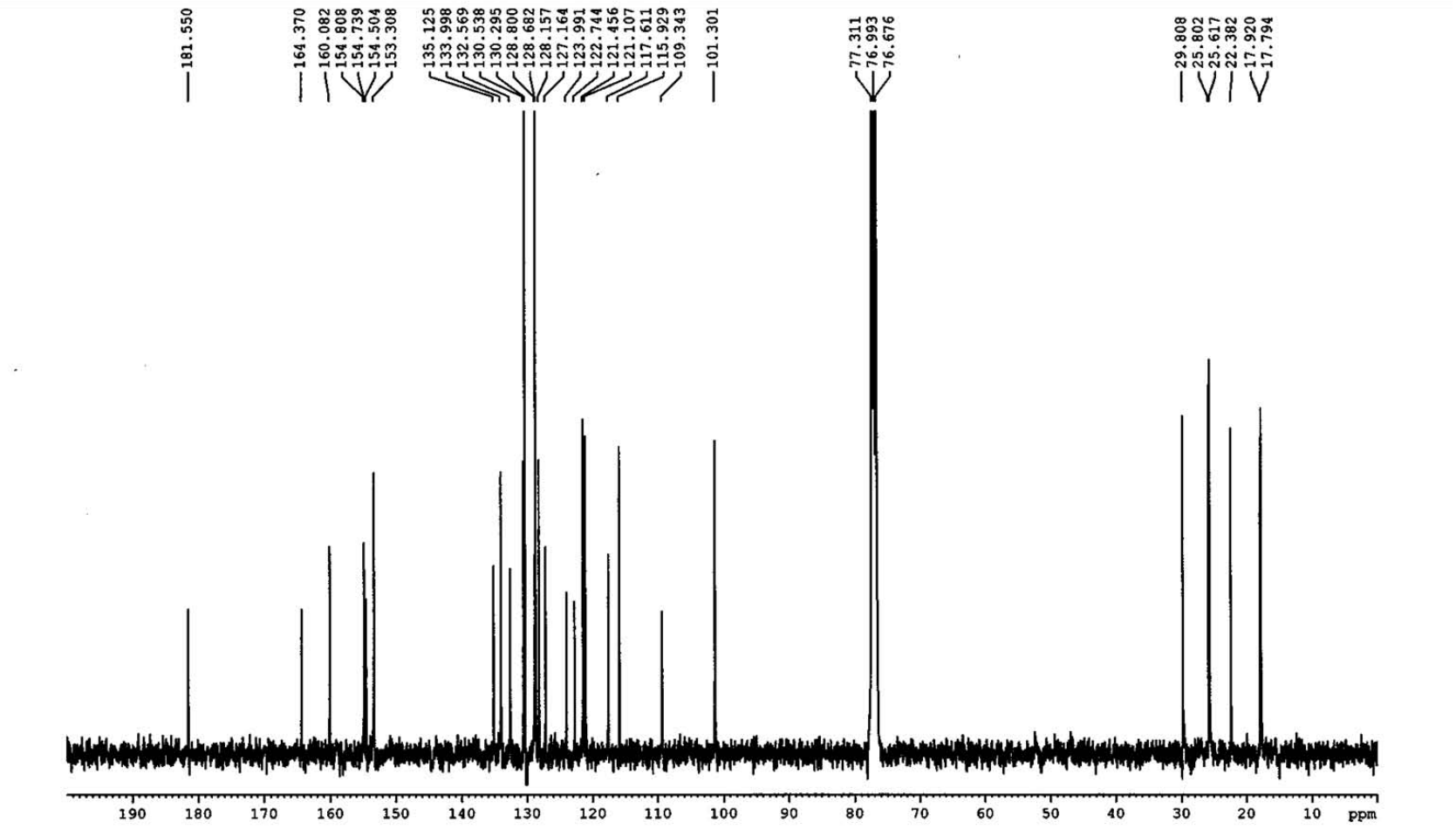


Figure 35a ^{13}C-NMR Spectrum of Lupalbigenin 7-*O*-benzoate (**150**) in $CDCl_3$

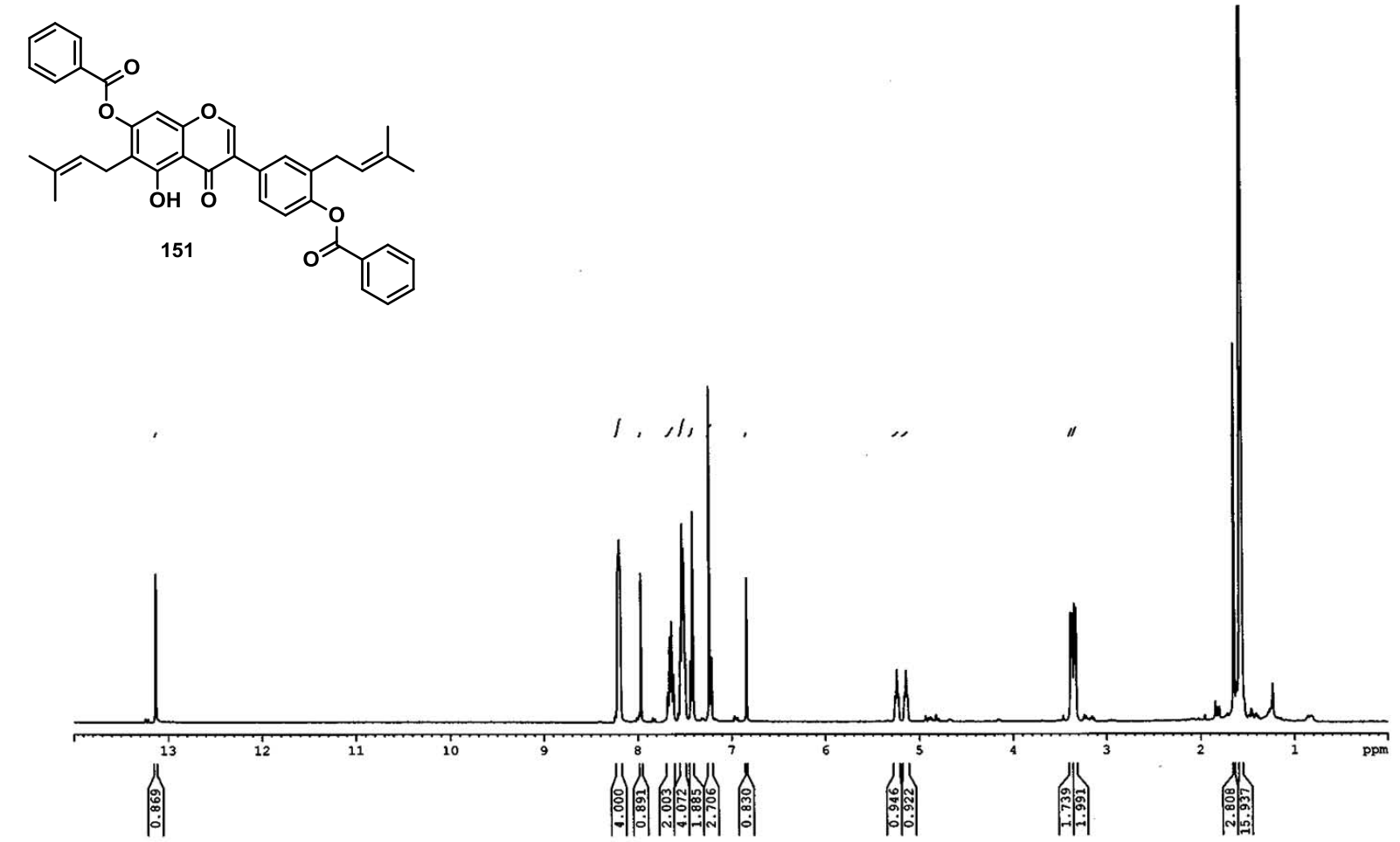


Figure 36 ^{1}H-NMR Spectrum of Lupalbigenin 7,4′-di-*O*-benzoate (**151**) in $CDCl_3$

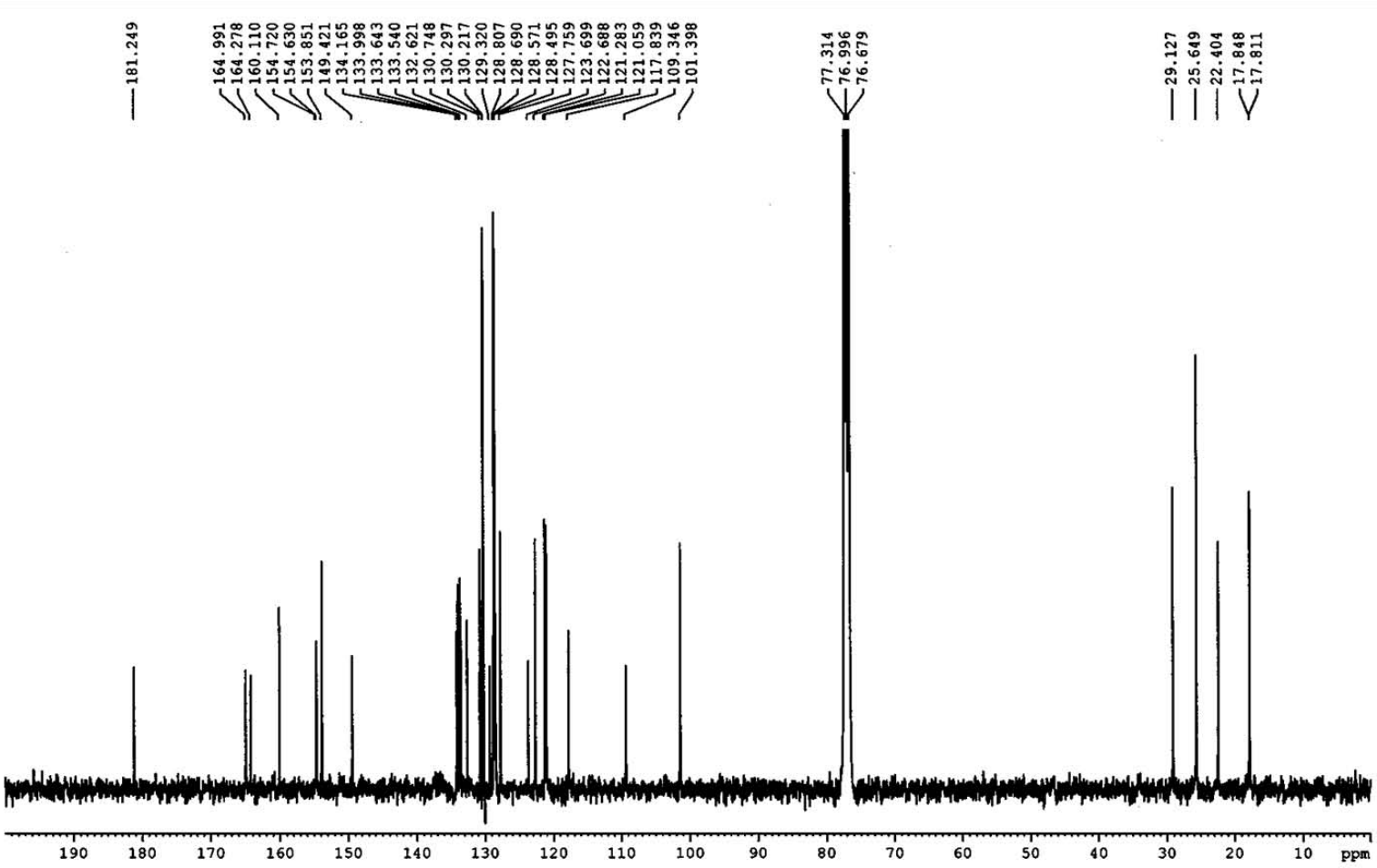


Figure 36a ^{13}C-NMR Spectrum of Lupalbigenin 7,4′-di-*O*-benzoate (**151**) in $CDCl_3$

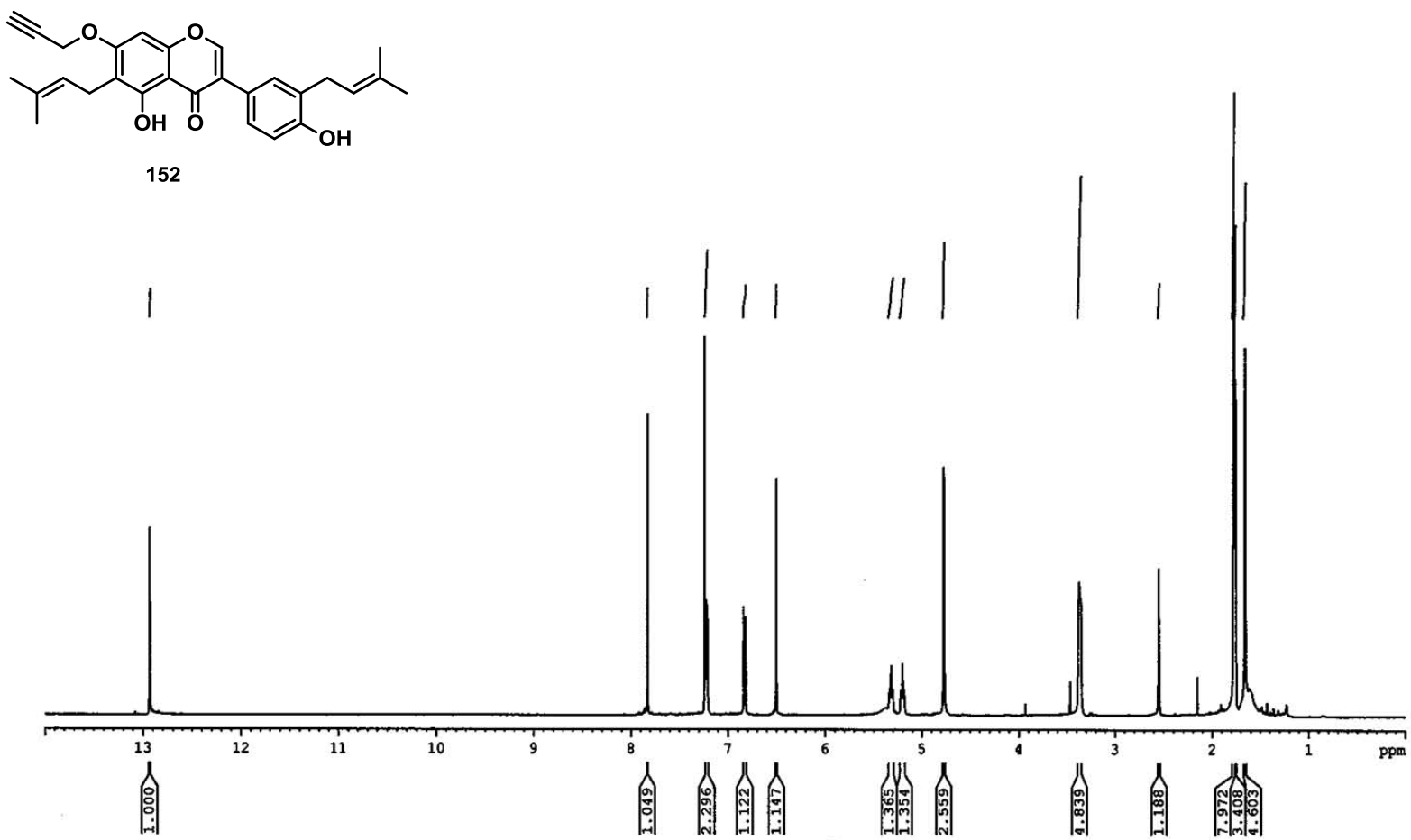


Figure 37 ^{1}H-NMR Spectrum of 7-*O*-Propargyllupalbigenin (**152**) in $CDCl_3$

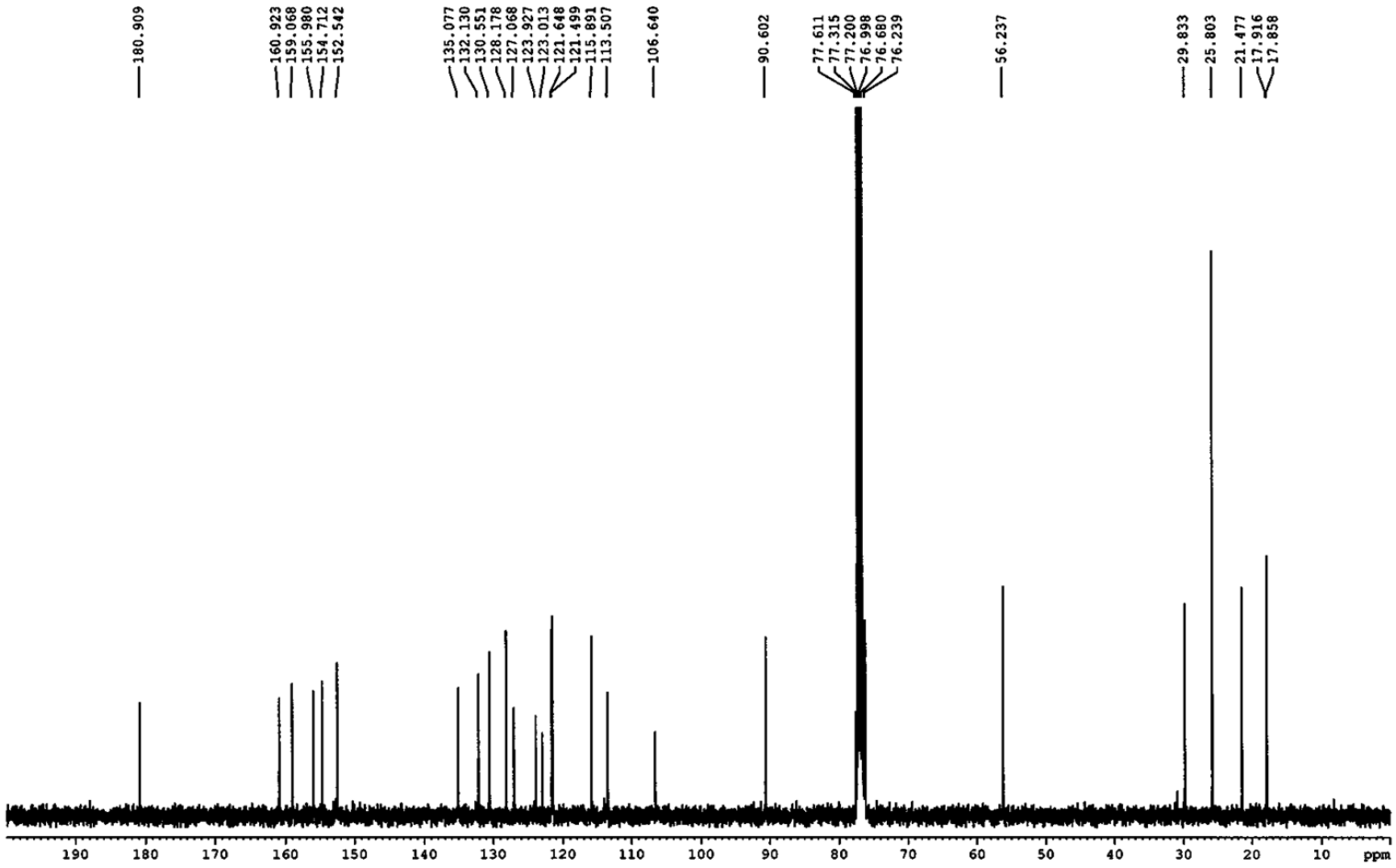
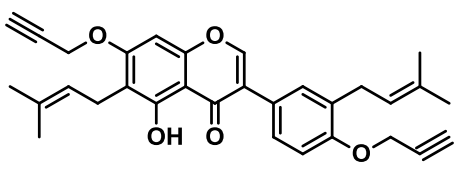


Figure 37a ^{13}C-NMR Spectrum of 7-*O*-Propargyllupalbigenin (**152**) in $CDCl_3$



153

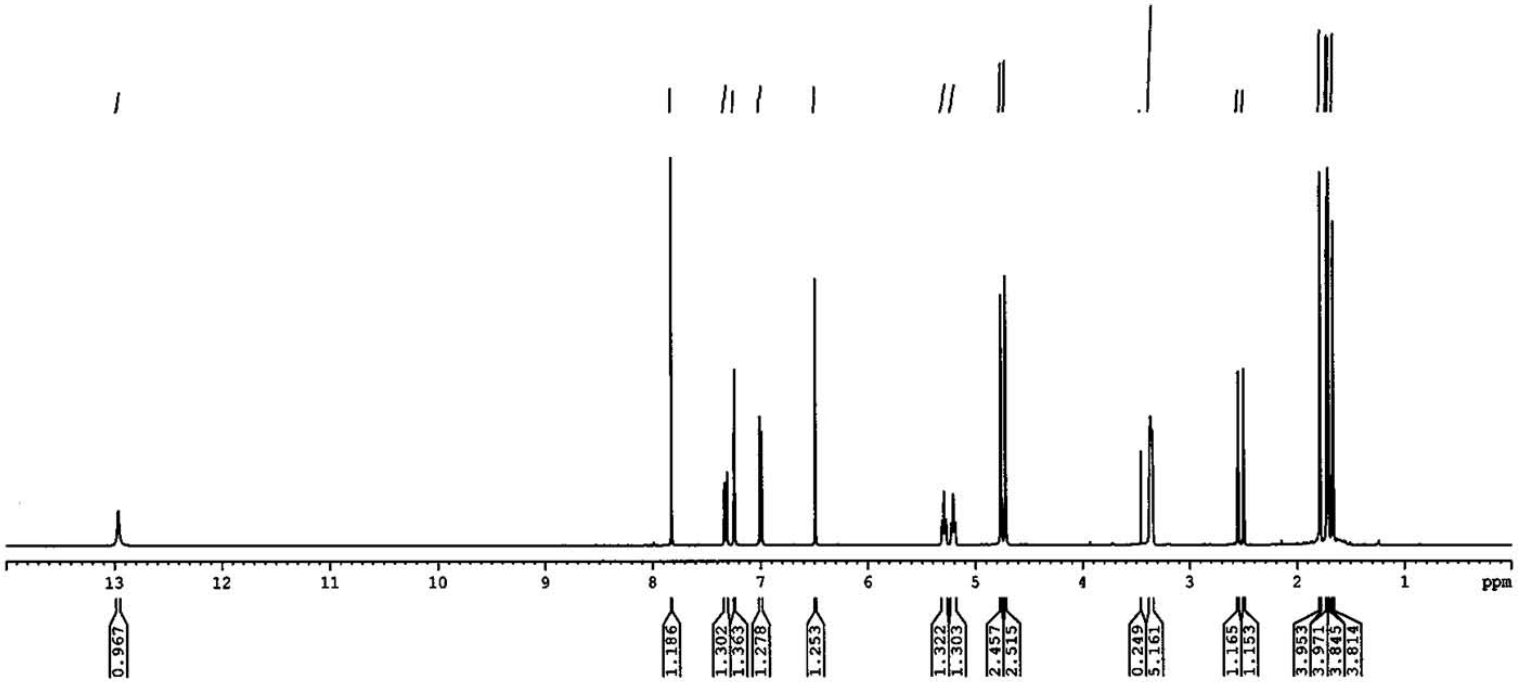


Figure 38 ^{1}H-NMR Spectrum of 7,4′-Di-*O*-propargyllupalbigenin (**153**) in $CDCl_3$

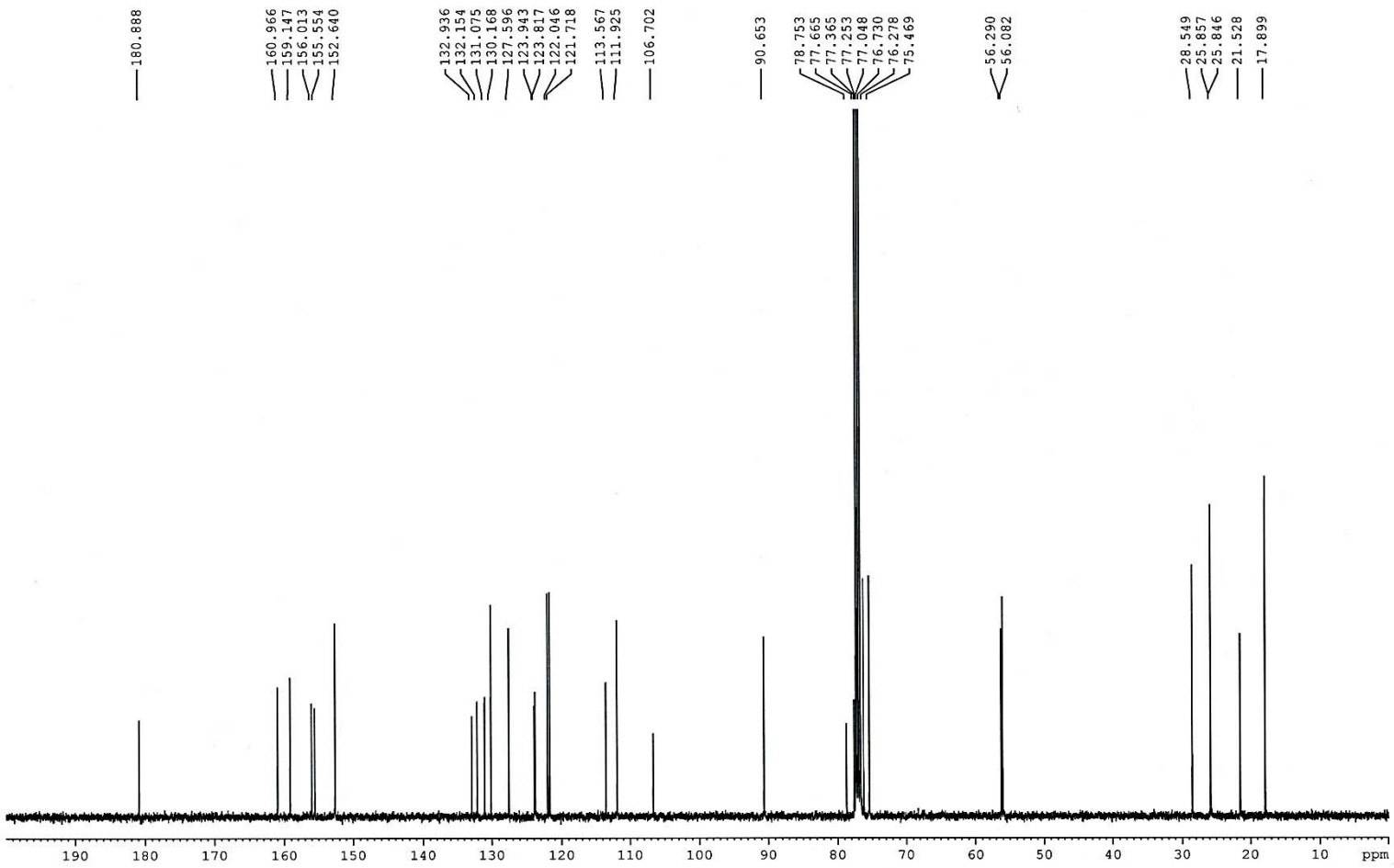


Figure 38a ^{13}C-NMR Spectrum of 7,4′-Di-*O*-propargyllupalbigenin (**153**) in $CDCl_3$

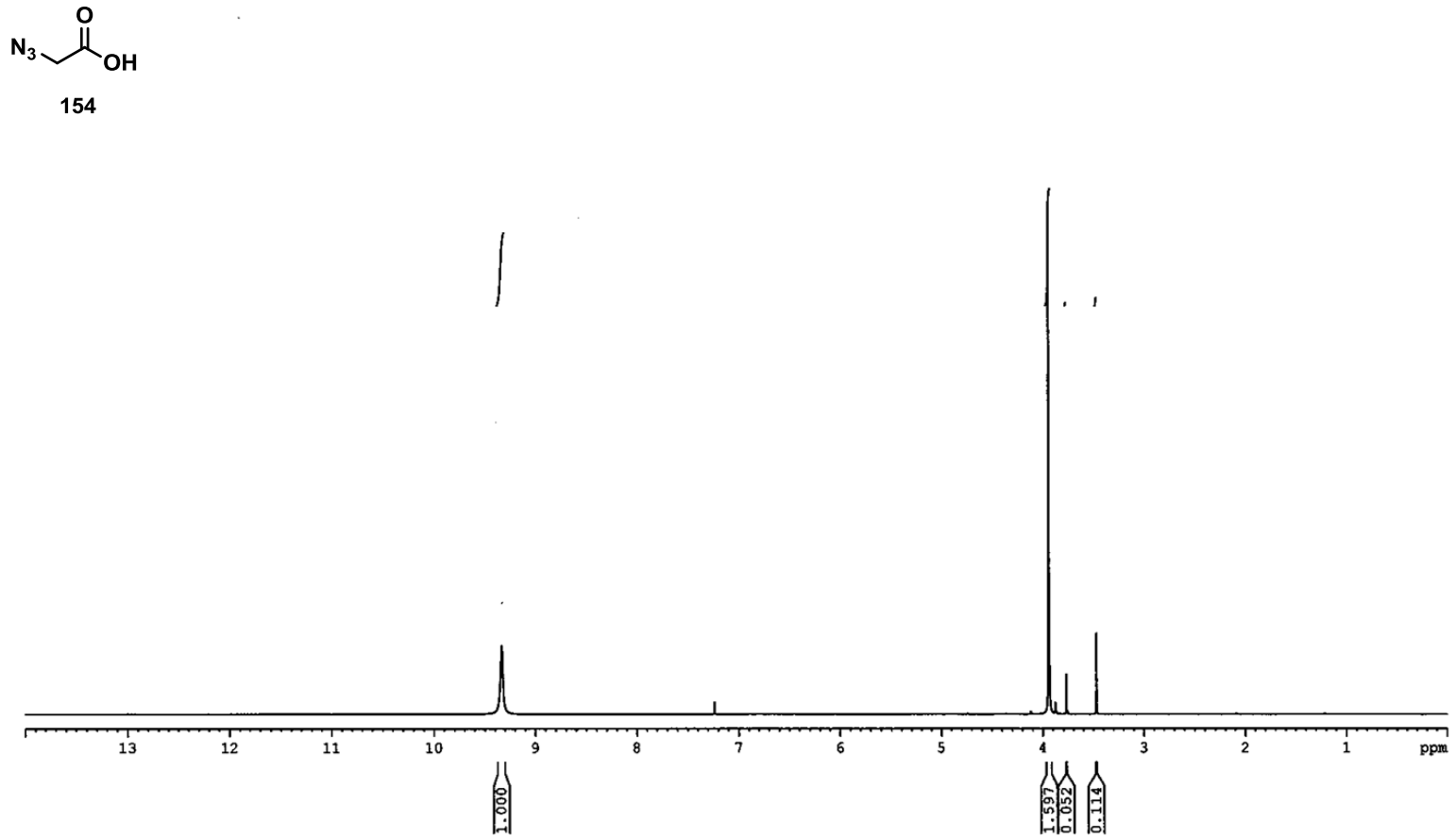


Figure 39 ^{1}H-NMR Spectrum of 2-Azidiacetic acid (**154**) in $CDCl_3$

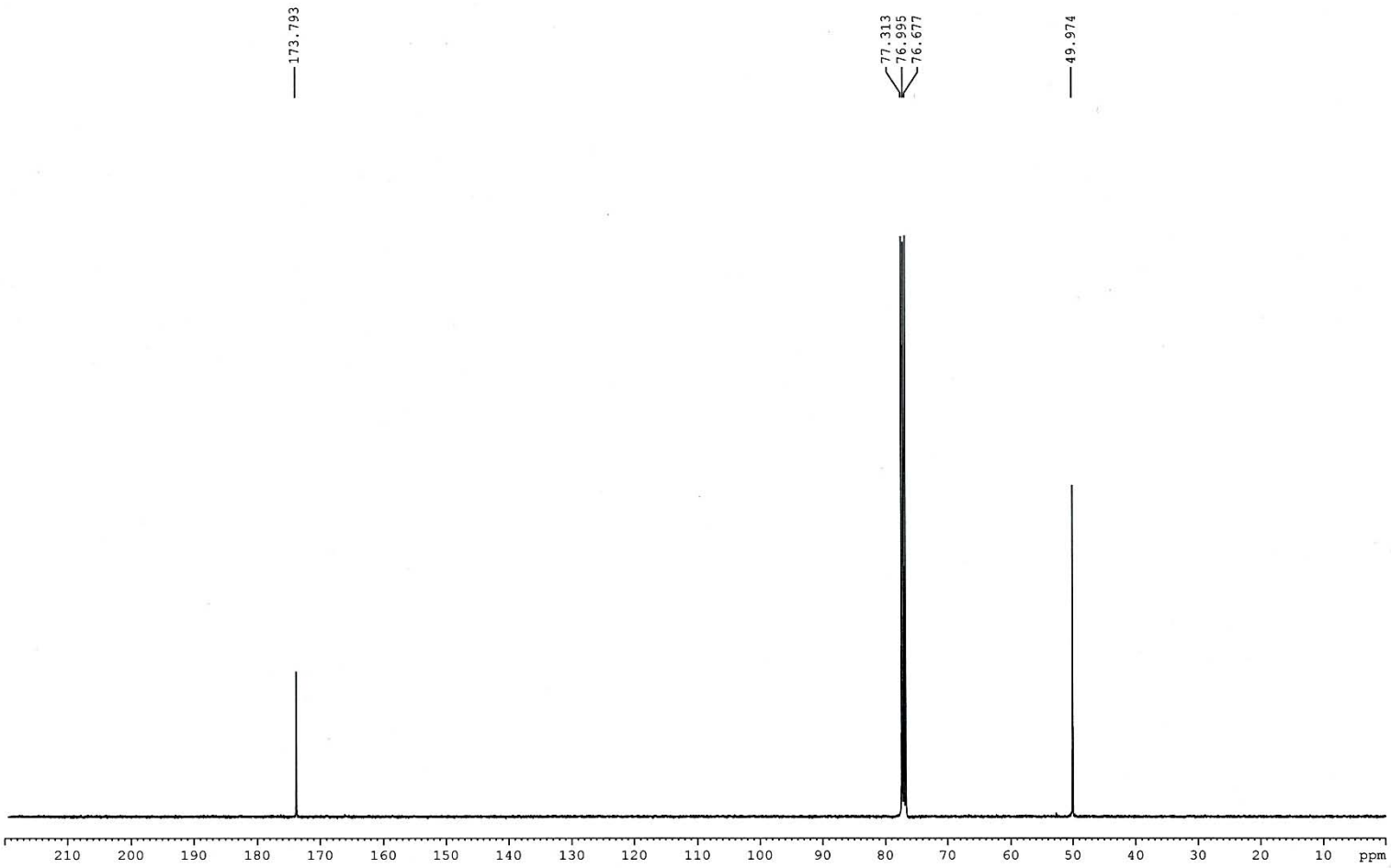


Figure 39a ^{13}C-NMR Spectrum of 2-Azidiacetic acid (**154**) in $CDCl_3$

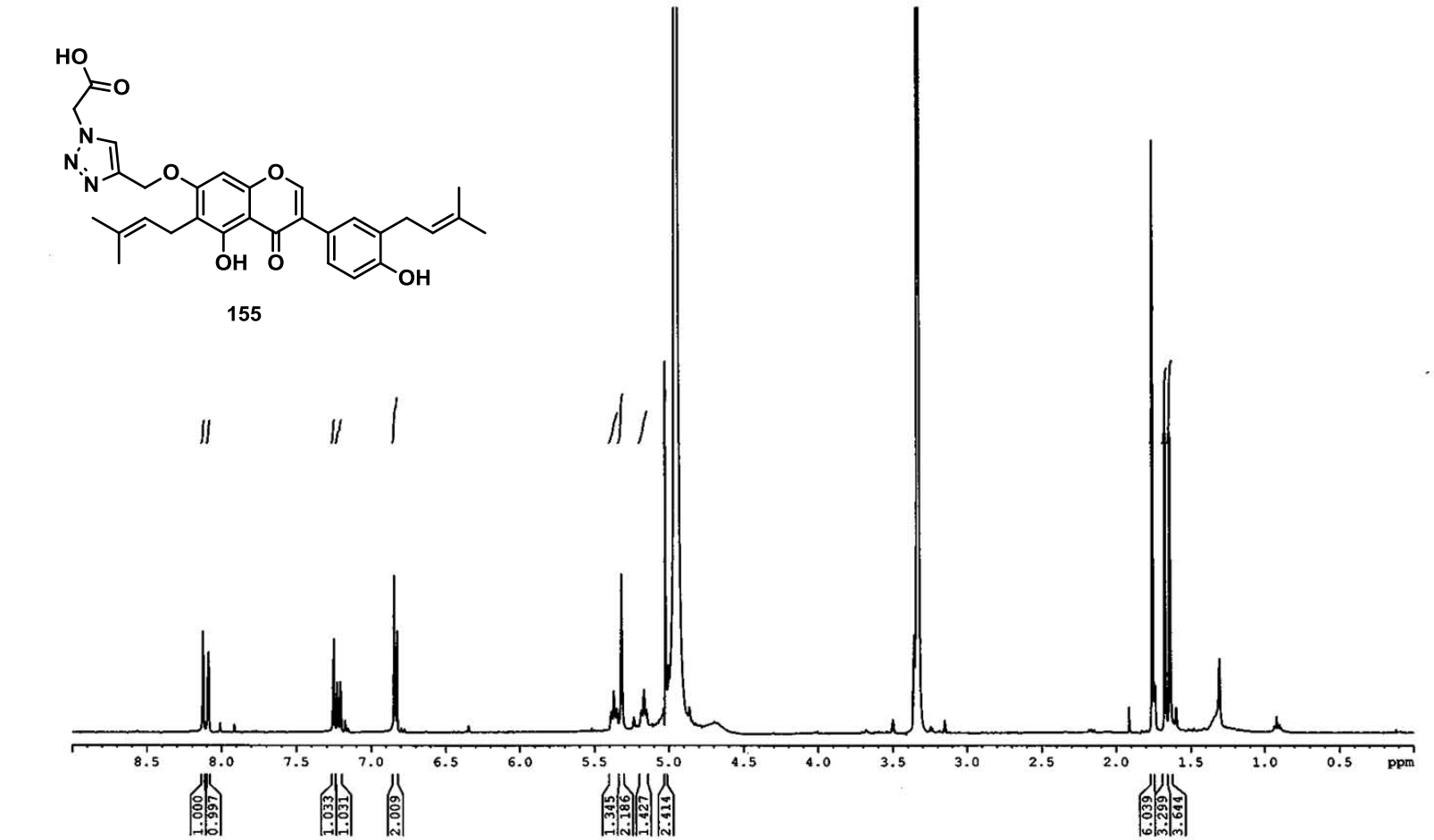


Figure 40 ^{1}H-NMR Spectrum of 7-*O*-[1′′′′-(Carboxymethyl)-1′′′′,*H*-3′′′′,4′′′′,5′′′′-triazole]lupalbigenin (**155**) in CD_3OD

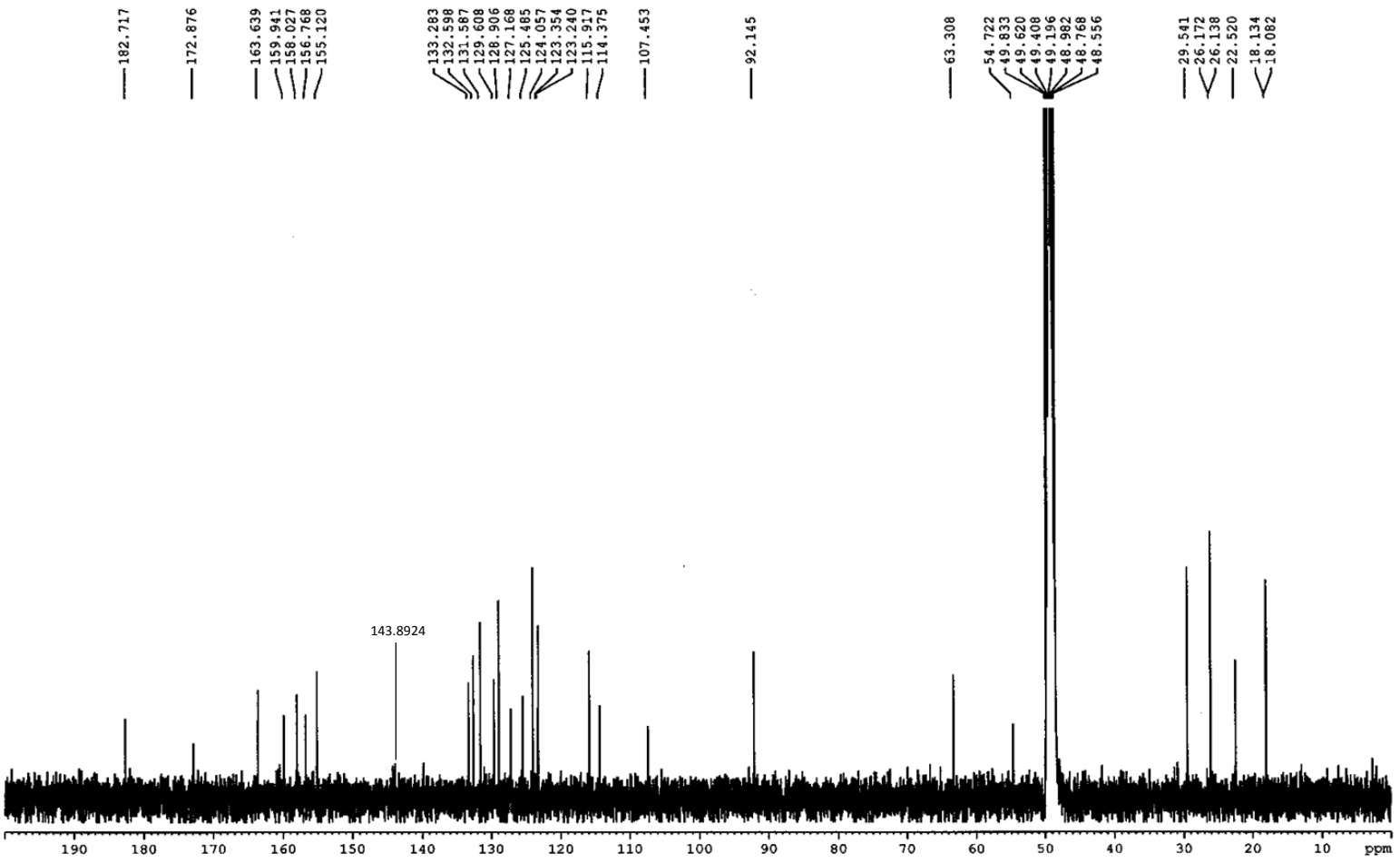


Figure 40a ^{13}C-NMR Spectrum of 7-*O*-[1′′′′-(Carboxymethyl)-1′′′′,*H*-3′′′′,4′′′′,5′′′′-triazole]lupalbigenin (**155**) in CD_3OD

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