

การศึกษาทางพุทธเคมีของลำต้นกล้วยฤาษี



นางสาวอรรวรรณ เทียรรัมย์พงษ์

สถาบันวิทยบริการ

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PHYTOCHEMICAL STUDY OF *DIOSPYROS GLANDULOSA* LACE STEMS

Miss Orawan Theanphong



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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for the Degree of Master of Science in Pharmaceutical Botany

Department of Pharmaceutical Botany

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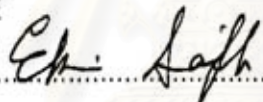
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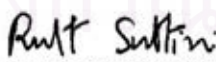

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จากส่วนลำต้นของกล้วยถั่ว (*Diospyros glandulosa* Lace) สามารถแยกสารในกลุ่มไตรเทอร์ปีนอยด์ได้ 6 ชนิด คือ friedelin, β - amyrin, lupeol, betulin, ursolic acid และ oleanolic acid การพิสูจน์เอกลักษณ์ของสารเหล่านี้ ทำโดยการวิเคราะห์ข้อมูล IR, MS, $^1\text{H-NMR}$ และ $^{13}\text{C-NMR}$ ร่วมกับการเปรียบเทียบกับค่าที่ได้มีการรายงานไว้แล้ว



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ลายมือชื่อนิสิต.....
 ลายมือชื่ออาจารย์ที่ปรึกษา.....
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From the stems of *Diospyros glandulosa* Lace, six triterpenoids: friedelin, β -amyrin, lupeol, betulin, ursolic acid and oleanolic acid have been isolated. Identification of these compounds was accomplished by analysis of their IR, MS, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ data as well as comparison with reported values.



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ABBREVIATIONS

br	=	broad
°C	=	degree Celsius
CC	=	column chromatography
CDCl ₃	=	deuterated chloroform
CHCl ₃	=	chloroform
cm	=	centimeter
¹³ C-NMR	=	Carbon-13 Nuclear Magnetic Resonance
COSY	=	Correlated Spectroscopy
δ	=	chemical shift
1-D	=	one dimensional
2-D	=	two dimensional
<i>d</i>	=	doublet
<i>dd</i>	=	doublet of doublets
DEPT	=	Distortionless Enhancement by Polarization Transfer
DMSO- <i>d</i> ₆	=	deuterated dimethylsulfoxide
EIMS	=	Electron Impact Mass Spectroscopy
EtOH	=	ethanol
eV	=	electron volt
g	=	gram
¹ H-NMR	=	Proton Nuclear Magnetic Resonance
HETCOR	=	Heteronuclear Correlation Spectroscopy
Hz	=	Hertz
IR	=	Infrared
<i>J</i>	=	coupling constant
KBr	=	potassium bromide
L	=	liter
<i>m</i>	=	multiplet
m	=	meter

M^+	=	molecular ion
MeOH	=	methanol
mg	=	milligram
MHz	=	Megahertz
ml	=	milliliter
mm	=	millimeter
MS	=	Mass Spectrum
m/z	=	mass-to-charge ratio
nm	=	nanometer
NMR	=	Nuclear Magnetic Resonance
ppm	=	part per million
<i>q</i>	=	quartet
rel. int.	=	relative intensity
<i>s</i>	=	singlet
sp.	=	species
<i>t</i>	=	triplet
TLC	=	Thin-Layer Chromatography
var.	=	variety
ν_{\max}	=	wavenumber at maximum absorption

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CHAPTER I

INTRODUCTION

Diospyros is numerically and economically the most important genus of Ebenaceae. The genus comprises about 400 species widespread chiefly in tropical areas and a few can be found in subtropical areas. (Phengklai, 1981)

Plants in the genus *Diospyros* are usually trees or shrubs, dioecious or sometimes monoecious or polygamous. All parts of these plants often turn blackish when dry. The leaves are distichous and mostly reflexed, penninerved. The inflorescences are cymose or fasciculate, axillary or ramiflorous, rarely cauliflorous, or the flowers are solitary. These flowers are actinomorphic. The calyx is more or less deeply lobed, persistent and usually accrescent in fruit; the lobes are valvate or imbricate in bud. The corolla is gamopetalous, caducous; its segments are patent and contorted in bud. The number of stamens is at least 6. The stamens are free or in pairs, inserted on the base of the corolla-tube, or in bundles on the receptacle. The anthers are basifixed, 2-locular, longitudinally dehiscent. Rudimentary ovary is usually present in male flowers, whereas staminodes are usually present in female flowers. The ovary is superior, (3-) 4 (-16)-locular with 1(-2) pendulous ovules in each locule. The numbers of styles are 1-5. The fruit is indehiscent, fleshy, dry or woody, one to many-seeded with ruminant or smooth endosperm (Phengklai, 1981).

The species of *Diospyros* found in Thailand are as follows (กรมป่าไม้, สำนักงานวิชาการป่าไม้, ส่วนพฤกษศาสตร์ป่าไม้, 2544).

1. *Diospyros andamanica* var. *aequabilis* Bakh.
2. *D. apiculata* Hiern
3. *D. areolata* King & Gamble
4. *D. bambuseti* Fletcher
5. *D. bejaudii* Lec.
6. *D. borneensis* Hiern
7. *D. brandisiana* Kurz

8. *D. buxifolia* (Bl.) Hiern
9. *D. castanea* Fletcher
10. *D. cauliflora* Bl.
11. *D. coetanea* (Craib) Fletcher
12. *D. collinsae* Craib
13. *D. confertiflora* (Hiern) Bakh.
14. *D. curranii* Merr.
15. *D. curraniopsis* Bakh.
16. *D. dasyphylla* Kurz
17. *D. decandra* Lour.
18. *D. dictyoneura* Hiern
19. *D. diepenhorstii* Miq.
20. *D. dumetorum* W. W. Sm
21. *D. ehretioides* Wall. ex G. Don
22. *D. ferrea* (Willd.) Bakh. var. *ferrea* (Willd.) Bakh.
23. *D. ferrea* (Willd.) Bakh. var. *littorea* (R.Br.) Bakh.
24. *D. filipendula* Pierre ex Lec.
25. *D. frutescens* Bl.
26. *D. fulvopilosa* Fletcher
27. *D. glandulosa* Lace
28. *D. gracilis* Fletcher
29. *D. hasseltii* Zoll.
30. *D. insidiosa* Bakh.
31. *D. kaki* L.*
32. *D. kerrii* Craib
33. *D. kurzii* Hiern
34. *D. lanceifolia* Roxb.
35. *D. latisepala* Ridl.
36. *D. longipilosa* Phengklai
37. *D. malabarica* (Desr.) Kostel. var. *malabarica* Kostel.
38. *D. malabarica* (Desr.) Kostel. var. *siamensis* (Hochr.) Phengklai

39. *D. martabanica* Clarke
40. *D. mollis* Griff.
41. *D. montana* Roxb.
42. *D. oblonga* Wall. ex G. Don
43. *D. pendula* Hasselt ex Hassk.
44. *D. philippensis* A.DC.*
45. *D. pilosanthera* Blanco
46. *D. pilosula* (A. DC.) Hiern
47. *D. pubicalyx* Bakh.
48. *D. pyrrhocarpa* Miq.
49. *D. rhodocalyx* Kurz
50. *D. rubra* Lec.
51. *D. scalariformis* Fletcher
52. *D. scortechinii* King & Gamble
53. *D. sumatrana* Miq.
54. *D. tahanensis* Bakh.
55. *D. thaiensis* Phengklai
56. *D. toposia* Ham. var. *toposia* Ham.
57. *D. toposia* Ham. var. *toposoides* (King & Gamble) Phengklai
58. *D. transitoria* Bakh.
59. *D. trianthos* Phengklai
60. *D. truncata* Zoll. & Moritzi
61. *D. undulata* Wall. ex G. Don var. *cratericalyx* (Craib) Bakh.
62. *D. undulata* Wall. ex G. Don var. *undulata* Wall.
63. *D. variegata* Kurz
64. *D. venosa* Wall ex. A. DC.
65. *D. wallichii* King & Gamble ex King
66. *D. winitii* Fletcher

* exotic plant

Diospyros glandulosa Lace is an evergreen or partly deciduous tree that can grow up to 15 m and is commonly found in hill forests. The stem bark is dark gray-brown or red-brown, shallowly to quite deeply cracked. The leaves are narrowly elliptic-oblong, 8-18 by 3-6.5 cm, with broadly tapering tip and slightly pointed or blunt base. The young leaves are densely coated with golden-brown hairs, mature leaves are smooth or with scattered dark brown hairs on midvein above and densely pale brown hair below. The leaves have 4-7 pairs of curved, sunken side veins, above; with ladder-like tertiary veins. The male flowers are 4(-5)-merous, in cymose inflorescence. The calyx is campanulate, 4-6 mm long, divided nearly to the base, with long-hair on both sides. The corolla is urceolate 6-8 mm long, globose, divided to a quarter up to a third, glabrous on both sides except along the midline of lobes. The numbers of stamens are 14-30. The female flowers are 4-merous, solitary, larger than the males. The ovary is ovate-shaped, pubescent, 8-locular. The style is solitary, pubescent, with 4 stigmas. The fruit is a globose berry, 2.5-3.5 by 2.5-4 cm, yellow-orange, succulent, slightly sunken at both ends, densely coated with silky hairs. The fruiting calyx is 1.6-1.8 cm long, divided to the base, spreading and wavy, conspicuously veined tomentose on both sides. The seeds are dark-brown, in a star-shaped pattern, with smooth endosperm (Phengkhai, 1981; Gardner, 2000) (Figure 1).

Thai vernacular names of this plant are “Kluai ruesi” (Chiang Mai, Mae Hong Son) “Chan pa” (Chiang Mai), “Ma khuea thuean” (Loei) and “Le-ko-mo” (Karen -Chiang Mai) (กรมป่าไม้, สำนักงานวิชาการป่าไม้, ส่วนพฤกษศาสตร์ป่าไม้, 2544).

More than 130 *Diospyros* species have been subjected to chemical screening and a variety of compounds have been isolated. It is interesting to note that triterpenoids and naphthoquinones are widely found and present in almost all parts of the plant species. Several of these compounds have been found to be bioactive. (Mallavadhani, Panda and Rao, 1998).

Diospyros glandulosa Lace is one of *Diospyros* species with no previous report on phytochemical investigation. This study deals with the isolation of chemical constituents from the stems of this plant, as well as the identification of those compounds. The data obtained from the study might provide useful information on phytochemistry and chemotaxonomy of the plant genus.



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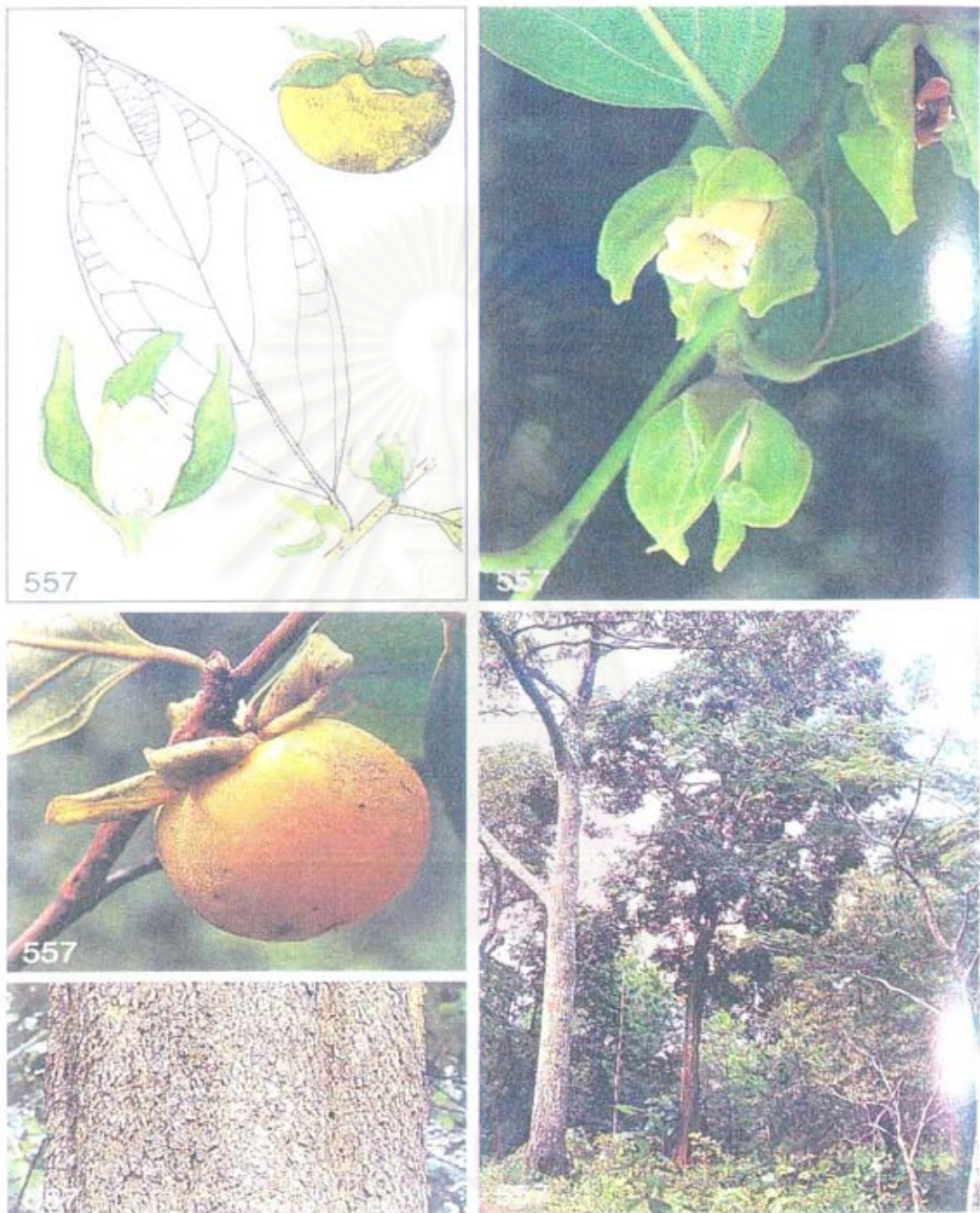


Figure 1. *Diospyros glandulosa* Lace (from Gardner, 2000)

CHAPTER II

HISTORICAL

Chemical Constituents of Plants in the Genus *Diospyros*

Plants in the genus *Diospyros* are found to contain a wide range of chemical constituents: naphthoquinones triterpenoids, steroids, flavonoids, coumarins, tannins and other miscellaneous substances. Two major groups of compounds which have been found widespread and present in almost all parts of the plants are naphthoquinones and triterpenoids. The occurrence of these compounds in *Diospyros* is summarized as follows.

1. Naphthoquinones

The *Diospyros* genus generates a large number of 1,4- metabolites belonging to the juglone class while only three 1,2- naphthoquinones have so far been found. The juglone - based 1,4-naphthoquinones include several monomers and dimers, together with a few trimers and tetramers. Almost all of them are derivatives of 7-methyljuglone and plumbagin, both of which are found to accumulate in significant quantities in a number of *Diospyros* species. These compounds can be used as chemical markers of the genus for taxonomic study.

The 1,4-naphthoquinones of *Diospyros* can be classified into two major groups: (A) monomeric naphthoquinones (including conjugated compounds with one molecule of naphthoquinone) and (B) oligomeric naphthoquinones.

1.1 Monomeric 1,4-naphthoquinones

About 25 metabolites of this group have so far been isolated. *D. melanoxylon* is found to be the potential source for substituted plumbagin (9-12). The partial quinone reduction products of plumbagin (isoshinanolone, 16) and 7-methyljuglone (shinanolone, 26) have been isolated from a few *Diospyros* plants, but the completely reduced quinone skeletons have not yet been detected in the genus.

1.2 Oligomeric 1,4-naphthoquinones

The majority of the *Diospyros* naphthoquinones are of this group and so far 43 oligomeric metabolites have been isolated. These oligomers are formed by coupling between (X) 7-methyljuglone monomers, (Y) plumbagin monomers and (Z) 7-methyljuglone and plumbagin monomers. Oligomers of type 3 are rare and so far only two compounds, ehretione (70) and habinone (71), have been found.

The distribution of naphthoquinones in the genus *Diospyros* is summarized in Table 1.



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Table 1. Distribution of naphthoquinones in the genus *Diospyros*

Compounds	Sources	References
1. 1,2-Naphthoquinones		
8-Hydroxy-1,2-naphthoquinone (1)	<i>D. tricolor</i>	Pista, 1954a; Pista, 1954b
3-Methyl-8-methoxy-1,2-naphthoquinone (2)	<i>D. melanoxylon</i>	Sidhu, Sankaram and Ali, 1968
6-Methyl-8-methoxy-1,2-naphthoquinone (3)	<i>D. celebica</i>	Maiti and Musgrave, 1986
2. 1,4-Naphthoquinones		
2.1 Monomeric 1,4-naphthoquinones		
2.1.1 Plumbagin and derivatives		
Plumbagin (4)	<i>D. canaliculata</i>	Zhong, Waterman and Jeffrey, 1984
	<i>D. ebenum</i>	Cooke and Dowd, 1952
	<i>D. elliptifolia</i>	Fallas and Thomson, 1968
	<i>D. gracilipes</i>	Thomson, 1971
	<i>D. greeniwayi</i>	Khan and Rwekika, 1998

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
Plumbagin (4)	<i>D. hebecarpa</i>	Cooke and Dowd, 1952; Cooke, Dowd and Webb, 1952
	<i>D. kaki</i>	Tezuka, <i>et al.</i> , 1972
	<i>D. maritima</i>	Tezuka, <i>et al.</i> , 1973
	<i>D. mesfiliformis</i>	Lajubutu, <i>et al.</i> , 1995
	<i>D. novoguianensis</i>	Khan and Timi, 1999b
	<i>D. olen</i>	Evans, <i>et al.</i> , 1999
	<i>D. siamang</i>	Zakaria, <i>et al.</i> , 1984
	<i>D. siderophylla</i>	Li, Lu and Zhong, 1981
	<i>D. walkeri</i>	Herath, 1978
	<i>D. wallichii</i>	Zakaria, <i>et al.</i> , 1984
3-Hydroxyplumbagin (5) (Droserone)	<i>D. maritima</i>	Higa, <i>et al.</i> , 1987
3-Chloroplumbagin (6)	<i>D. maritima</i>	Higa, <i>et al.</i> , 1987

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
3-Bromoplumbagin (7)	<i>D. maritima</i>	Higa, <i>et al.</i> , 1987
Methylnaphthazarin (8)	<i>D. heterotricha</i> <i>D. lycioides</i>	Ferreira, Costa and Alves, 1972 ; Van Der Vijver and Gerritsma, 1974 Van Der Vijver and Gerritsma, 1974
2-Methyl-5-methoxy-1,4-naphthoquinone (9)	<i>D. melanoxylon</i>	Sidhu, <i>et al.</i> , 1968
2-Methyl-3-hydroxy-5-methoxy-1,4-naphthoquinone (10)	<i>D. melanoxylon</i>	Sidhu, <i>et al.</i> , 1968

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
2-Methyl-5-methoxy-6-hydroxy -1,4-naphthoquinone (11) (Diomelaquinone)	<i>D. celebica</i> <i>D. melanoxylon</i>	Maiti and Musgrave, 1986 Sidhu, <i>et al.</i> , 1968
2-Methyl-5,6-dimethoxy-1,4-naphthoquinone (12)	<i>D. melanoxylon</i>	Sidhu, <i>et al.</i> , 1968
Canaliculatin (13)	<i>D. canaliculata</i>	Jeffreys and Zakaria, 1983; Zhong, <i>et al.</i> , 1984
Cyclocanaliculatin (14)	<i>D. canaliculata</i>	Jeffreys and Zakaria, 1983; Zhong, <i>et al.</i> , 1984
Ebenone (15)	<i>D. ebenum</i>	Sankaram and Reddy, 1984

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
Isoshinanolone (16)	<i>D. maritima</i> <i>D. samoensis</i> <i>D. siamang</i> <i>D. wallichii</i>	Tezuka, <i>et al.</i> , 1973 Richomme, <i>et al.</i> , 1991 Zakaria <i>et al.</i> , 1984 Zakaria <i>et al.</i> , 1984
Epi-isoshinanolone (17)	<i>D. canaliculata</i>	Zhong, <i>et al.</i> , 1984
2.1.2 7-Methyljuglone and derivatives		
7-Methyljuglone (18)	<i>D. alboflavescena</i> <i>D. austro-africana</i> <i>D. chloroxylon</i> <i>D. ebenaster</i> <i>D. ebenum</i> <i>D. ferrea</i> <i>D. fischeri</i>	Bouquet, 1973 Van Der Vijver and Gerritsma, 1974 Sidhu and Prasad, 1967 Dominguez <i>et al.</i> , 1979 Ruzicka, Eschenmoser and Heusser, 1953 Tezuka <i>et al.</i> , 1973 Khan and Rwekika, 1992

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
7-Methyljuglone (18)	<i>D. gilleti</i> <i>D. greeniwayi</i> <i>D. guianensis</i> <i>D. hallierii</i> <i>D. heterotricha</i> <i>D. hoyleana</i> <i>D. inhacaensis</i> <i>D. ismailii</i> <i>D. kaki</i> <i>D. lotus</i> <i>D. lycioides</i> <i>D. mafiensis</i> <i>D. mannii</i> <i>D. melanoxylon</i> <i>D. montana</i>	Bouquet, 1973 Khan and Rwekika, 1998 Braneton and Moretti, 1979 Khan and Timi, 1999a Ferreira, Alves and Sousa, 1974 Bouquet, 1973 Van Der Vijver and Gerritsma, 1974 Zakaria <i>et al.</i> , 1984 Tezuka <i>et al.</i> , 1972; Lin, Chou and Chen, 1988 Yoshihira, Tezuka and Natori, 1971; Hasan, Matyikhina and Saltykova, 1975 Cai <i>et al.</i> , 2000 Khan and Rwekika, 1992 Jeffreys, Zakaria and Waterman, 1983 Row, Sundar Ramaiah and Rao, 1965 Lillie, Musgrave and Skoules, 1976a

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
7-Methyljuglone (18)	<i>D. moonii</i> <i>D. natalensis</i> <i>D. nicaragunensis</i> <i>D. novoguianensis</i> <i>D. rotundifolia</i> <i>D. squarrosa</i> <i>D. sumatrana</i> <i>D. usambarensis</i> <i>D. verrucosa</i> <i>D. virginiana</i> <i>D. whyteana</i> <i>D. zombensis</i>	Waterman and Mbi, 1979 Van Der Vijver and Gerritsma, 1974 Husbun, <i>et al.</i> , 1988 Khan and Timi, 1999b Van Der Vijver and Gerritsma, 1974 Khan, Nkunya and Wevers, 1979 Zakaria, <i>et al.</i> , 1984 Marston, Msonthi and Hostettmann, 1984; Kahn, Kishimba and Locksley, 1989 Khan, Kishimba and Locksley, 1987 Carter, Garlo and Stanley, 1978 Tannock, 1973 Gafner <i>et al.</i> , 1987; Gafner and Rodriguez, 1988
2-Methoxy-7-methyljuglone (19)	<i>D. usambarensis</i>	Marston, Msonthi and Hostettmann, 1984

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
3-Methoxy-7-methyljuglone (20)	<i>D. kaki</i>	Yoshihira, Tezuka and Kanchanapee, 1971
	<i>D. usambarensis</i>	Marston, <i>et al.</i> , 1984
Celebaquinone (21)	<i>D. celebica</i>	Maiti and Musgrave, 1986
Isocelebaquinone (22)	<i>D. celebica</i>	Maiti and Musgrave, 1986
Chromenone acid (23)	<i>D. montana</i>	Lillie, <i>et al.</i> , 1976a
Chromenone ester (24)	<i>D. montana</i>	Lillie, <i>et al.</i> , 1976a
Ismailin (25)	<i>D. ismailii</i>	Jeffreys and Zakaria, 1983 ; Waterman <i>et al.</i> , 1985
Shinanolone (26)	<i>D. kaki</i>	Tezuka, <i>et al.</i> , 1972; Lin, Chou and Chen, 1988
	<i>D. kaki</i> var. <i>sylvestris</i>	Tezuka, <i>et al.</i> , 1972; Lin, <i>et al.</i> , 1988
	<i>D. maingayi</i>	Zakaria, <i>et al.</i> , 1984

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
Shinanolone (26)	<i>D. morrisiana</i>	Chen <i>et al.</i> , 1987
	<i>D. virginiana</i>	Carter, <i>et al.</i> , 1978
2.1.3 Miscellaneous		
3-Methoxyjuglone (27)	<i>D. morrisiana</i>	Chen <i>et al.</i> , 1987
Yerrinquinone (28)	<i>D. montana</i>	Pardhasaradhi and Rao, 1990
2.2 Oligomeric 1,4-naphthoquinones		
2.2.1 Derivatives of plumbagin monomers		
Elliptinone (29)	<i>D. ebenum</i>	Sankaram and Reddy, 1984
	<i>D. elliptifolia</i>	Fallas and Thomson, 1968
	<i>D. ehretioides</i>	Lillie, Musgrave and Skoyles, 1976b
	<i>D. maritima</i>	Tezuka, <i>et al.</i> , 1973

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
Elliptinone (29)	<i>D. mollis</i> <i>D. samoensis</i> <i>D. siamang</i> <i>D. walkeri</i> <i>D. wallichii</i>	Yoshihira, <i>et al.</i> , 1971a Richomme, <i>et al.</i> , 1991 Zakaria, <i>et al.</i> , 1984 Herath, <i>et al.</i> , 1987 Zakaria <i>et al.</i> , 1984
Elliptinone dimethyl ester (30)	<i>D. mollis</i>	Yoshihira, <i>et al.</i> , 1971a
Undulatanone (31)	<i>D. undulata</i> var. <i>cratericalyx</i>	Aoonpakh, 2001
Maritinone (32)	<i>D. kaki</i> <i>D. maritima</i> <i>D. samoensis</i>	Yoshihira, <i>et al.</i> , 1971c Tezuka, <i>et al.</i> , 1973 ; Higa, 1998 Richomme, <i>et al.</i> , 1991
3-8'-Biplumbagin (33)	<i>D. greeniwayi</i>	Khan and Rwekika, 1999

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
3,3'-Dimer of 6-hydroxy-5-methoxy-2-methyl-1,4-naphthoquinone (34)	<i>D. melanoxylon</i>	Sidhu, Sankaram and Ali, 1973
Ethylidene-6,6'-biplumbagin (35)	<i>D. maritima</i>	Higa, 1988
<p>2.2.2 Derivatives of 7-methyljuglone monomers</p> <p>Diospyrin (36)</p>	<p><i>D. abyssinica</i></p> <p><i>D. chamaethammus</i></p> <p><i>D. chloroxylon</i></p> <p><i>D. cinnabarina</i></p> <p><i>D. fragrans</i></p> <p><i>D. gracilescens</i></p> <p><i>D. kamerunensis</i></p> <p><i>D. kaki</i></p> <p><i>D. longiflora</i></p>	<p>Zhong, <i>et al.</i>, 1984</p> <p>Costa, <i>et al.</i>, 1998</p> <p>Sidhu and Prasad, 1967</p> <p>Waterman and Mbi, 1979</p> <p>Zhong, <i>et al.</i>, 1984</p> <p>Waterman and Mbi, 1979</p> <p>Zhong, <i>et al.</i>, 1984</p> <p>Tezuka, <i>et al.</i>, 1972; Lin <i>et al.</i>, 1988</p> <p>Zhong, <i>et al.</i>, 1984</p>

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
Diospyrin (36)	<i>D. lotus</i> <i>D. mannii</i> <i>D. maritima</i> <i>D. obliquifolia</i> <i>D. piscatoria</i> <i>D. rotundifolia</i> <i>D. spinescens</i> <i>D. virginiana</i>	Tezuka, <i>et al.</i> , 1973 Jeffreys, <i>et al.</i> , 1983 Kuo, <i>et al.</i> , 1997a Sidhu and Prasad, 1967 Adeniyi, <i>et al.</i> , 2000 Van Der Vijver and Gerritsma, 1974 Herath <i>et al.</i> , 1978 Fallas and Thomson, 1968
8-Hydroxydiospyrin (37)	<i>D. maritima</i> <i>D. montana</i>	Kuo, <i>et al.</i> , 1997c Lillie, <i>et al.</i> , 1976a
3'-Methoxy diospyrin (38)	<i>D. mannii</i>	Jeffreys, <i>et al.</i> , 1983
2'-Chlorodiospyrin (39)	<i>D. montana</i>	Lillie, <i>et al.</i> , 1976a

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
3'-Chlorodiospyrin (40)	<i>D. montana</i>	Lillie, <i>et al.</i> , 1976a
3'-Chloro-2'-hydroydiospyrin (41)	<i>D. montana</i>	Lillie, <i>et al.</i> , 1976a
β' -Dihydrodiospyrin (42)	<i>D. montana</i>	Pardhasaradhi and Sidhu, 1972
Tetrahydrodiospyrin (43)	<i>D. montana</i>	Pardhasaradhi and Krishna Kumari, 1979
Cyclodiospyrin (44)	<i>D. montana</i>	Lillie, <i>et al.</i> , 1976a
Isodiospyrin (45)	<i>D. abyssinica</i>	Uphof, 1968
	<i>D. alboflavescena</i>	Bouquet , 1972
	<i>D. bipindensis</i>	Waterman and Mbi, 1979
	<i>D. chamaethamnus</i>	Costa <i>et al.</i> , 1998

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
Isodiospyrin (45)	<i>D. chloroxylon</i> <i>D. dendo</i> <i>D. ebenaster</i> <i>D. ferrea</i> <i>D. gilleti</i> <i>D. gracilescens</i> <i>D. greeniwayi</i> <i>D. hoyleana</i> <i>D. japonica</i> <i>D. kaki</i> <i>D. kaki</i> var. <i>sylvestris</i> <i>D. lotus</i> <i>D. lycioides</i> <i>D. mafiensis</i> <i>D. maingayi</i>	Sidhu and Prasad, 1967 Zhong, <i>et al.</i> , 1984 Dominguez, <i>et al.</i> , 1979 Tezuka <i>et al.</i> , 1973 Bouquet, 1973 Waterman and Mbi, 1979; Zhong, <i>et al.</i> , 1984 Khan and Rwekika, 1998 Bouquet, 1972 Tezuka <i>et al.</i> , 1973 Tezuka <i>et al.</i> , 1972; Lin, <i>et al.</i> , 1988 Tezuka <i>et al.</i> , 1972; Lin, <i>et al.</i> , 1988 Yoshihira, <i>et al.</i> , 1971a; Yoshihira, Tezuka and Natori, 1970b Van Der Vijver and Gerritsma, 1974 Khan and Rwekika, 1999 Zakaria <i>et al.</i> , 1984

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
Isodiospyrin (45)	<i>D. mespiliformis</i> <i>D. momtana</i> <i>D. morrisiana</i> <i>D. nicaraguensis</i> <i>D. piscatoria</i> <i>D. texana</i> <i>D. usambarensis</i> <i>D. verrucosa</i> <i>D. virginiana</i> <i>D. whyteana</i> <i>D. zombensis</i>	Fallas and Thomson, 1968 Lillie, <i>et al.</i> , 1976a Yoshihira, <i>et al.</i> , 1971; Yan, <i>et al.</i> , 1989 Choudhary, <i>et al.</i> , 1990 Adeniyi <i>et al.</i> , 2000 Dominiguez, <i>et al.</i> , 1979 Marston, <i>et al.</i> , 1984 Khan, <i>et al.</i> , 1987 Fallas, and Thomson, 1968 Tannock, 1973 Gafner <i>et al.</i> , 1987
8-Hydroxyisodiospyrin (46)	<i>D. ferrea</i> <i>D. heterotricha</i> <i>D. kaki</i> <i>D. lycioides</i>	Tezuka <i>et al.</i> , 1973 Ferreira, <i>et al.</i> , 1972 Tezuka <i>et al.</i> , 1973 Ferreira, <i>et al.</i> , 1972

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
2'-Methoxyisodiospyrin (47)	<i>D. morrisiana</i>	Chen <i>et al.</i> , 1987
3'-Methoxyisodiospyrin (48)	<i>D. morrisiana</i>	Chen <i>et al.</i> , 1987
3-Ethoxyisodiospyrin (49)	<i>D. maritima</i>	Kuo <i>et al.</i> , 1998a
2'-Ethoxyisodiospyrin (50)	<i>D. maritima</i>	Kuo <i>et al.</i> , 1998a
3'-Ethoxyisodiospyrin (51)	<i>D. maritima</i>	Kuo <i>et al.</i> , 1998b
8'-Hydroxy-3-methoxyisodiospyrin (52)	<i>D. morrisiana</i>	Chen <i>et al.</i> , 1987
2,2'-dimethoxyisodiospyrin (53)	<i>D. morrisiana</i>	Chen <i>et al.</i> , 1987
2,3'-dimethoxyisodiospyrin (54)	<i>D. morrisiana</i>	Chen <i>et al.</i> , 1987

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
3,3'-dimethoxyisodiospyrin (55)	<i>D. morrisiana</i>	Chen <i>et al.</i> , 1987
Biramentaceone (56)	<i>D. chamaethamnus</i>	Costa <i>et al.</i> , 1998
	<i>D. melanoxylon</i>	Sankaram and Sidhu, 1971 ; Sankaram , Reddy and Sidhu, 1981
	<i>D. novoguianensis</i>	Khan and Timi, 1999b
Rotundiquinone (57)	<i>D. ismailii</i>	Zakaria <i>et al.</i> , 1984
	<i>D. rotundifolia</i>	Maiti, Musgrave and Skoyles, 1976
Mamegakinone (58)	<i>D. chamaethamnus</i>	Costa <i>et al.</i> , 1998
	<i>D. japonica</i>	Tezuka <i>et al.</i> , 1973
	<i>D. kaki</i>	Tezuka <i>et al.</i> , 1972
	<i>D. lotus</i>	Yoshihira, <i>et al.</i> , 1971b
	<i>D. lycioides</i>	Li <i>et al.</i> , 1998
	<i>D. mollis</i>	Yoshihira, <i>et al.</i> , 1971a

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
Mamegakinone (58)	<i>D. montana</i> <i>D. obliquifolia</i> <i>D. usambarensis</i> <i>D. zombensis</i>	Yoshihira, <i>et al.</i> , 1971b Waterman and Mbi, 1979 Marston, <i>et al.</i> , 1984 Khan, <i>et al.</i> , 1989
Mamegakinone dimethyl ester (59)	<i>D. mollis</i>	Yoshihira, <i>et al.</i> , 1971a
Neodiospyrin (60)	<i>D. ismailii</i> <i>D. kaki</i> <i>D. lotus</i> <i>D. montana</i>	Zakaria <i>et al.</i> , 1984 Tezuka <i>et al.</i> , 1972 Tezuka <i>et al.</i> , 1973 Pardhasaradhi and Krishnakumari, 1979
Lemuninol A (61)	<i>Diospyros sp.</i>	Okuyama <i>et al.</i> , 1999

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
Diosquinone (62)	<i>D. chamaethamnus</i> <i>D. mafiensis</i> <i>D. mesfiliformis</i> <i>D. tricolor</i> <i>D. zombensis</i>	Costa <i>et al.</i> , 1998 Khan and Rwekika, 1992 Constanze <i>et al.</i> , 1998 Alake, 1994 Khan, Kishimba and Lockslay, 1987b
Batocanone (63)	<i>D. batocana</i>	Alves and Costa, 1980
Diosindigo A (64)	<i>D. bipindensis</i> <i>D. buxifolia</i> <i>D. caulifolia</i> <i>D. consolatae</i> <i>D. dendo</i> <i>D. ehretioides</i> <i>D. ferrea</i>	Waterman and Mbi, 1979 Musgrave and Skoyles, 1998 Musgrave and Skoyles, 1998 Khan, <i>et al.</i> , 1987 Zhong, <i>et al.</i> , 1984 Musgrave and Skoyles, 1974 Tezuka <i>et al.</i> , 1973

Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
Diosindigo A (64)	<i>D. fischeri</i> <i>D. hirsuta</i> <i>D. kaki</i> <i>D. kirkii</i> <i>D. lotus</i> <i>D. mafiensis</i> <i>D. maingayi</i> <i>D. melanoxylon</i> <i>D. moonii</i> <i>D. squarrosa</i> <i>D. sumatrana</i> <i>D. usambarensis</i> <i>D. variegata</i> <i>D. villosiuscula</i> <i>D. verrucosa</i> <i>D. zenkeri</i> <i>D. zombensis</i>	Khan and Rwekika, 1992 Herath, <i>et al.</i> , 1978 Tezuka <i>et al.</i> , 1973 Tezuka <i>et al.</i> , 1973; Khan and Rwekika, 1992 Khan and Rwekika, 1998 Khan and Rwekika, 1998 Musgrave and skoyles, 1974 Sankaram <i>et al.</i> , 1981 Herath <i>et al.</i> , 1978 Khan, <i>et al.</i> , 1987b Musgrave and Skoyles, 1974 Khan, <i>et al.</i> , 1989 Musgrave and Skoyles, 1974 Khan and Timi, 1999c Khan, <i>et al.</i> , 1987a Zhong <i>et al.</i> , 1984 Khan, <i>et al.</i> , 1987b

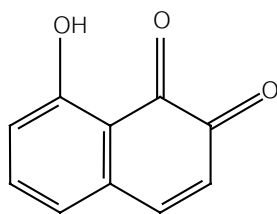
Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
Diosindigo B (65)	<i>D. celebica</i> <i>D. melanoxylon</i> <i>D. usambarensis</i> <i>D. villosiuscula</i>	Maiti, <i>et al.</i> , 1976 Sankaram, <i>et al.</i> , 1981 Khan, <i>et al.</i> , 1989 Khan and Timi, 1999c
Pentacyclic quinone (66)	<i>D. melanoxylon</i>	Sankaram, <i>et al.</i> , 1981
Xylospyrin (67)	<i>D. chamaethamnus</i> <i>D. chloroxylon</i> <i>D. ebenaster</i> <i>D. texana</i>	Costa <i>et al.</i> , 1998 Sidhu and Prasad, 1970 Dominguez, <i>et al.</i> , 1979 Dominguez, <i>et al.</i> , 1979
Bis-isodiospyrin (68)	<i>D. japonica</i> <i>D. lotus</i> <i>D. maingayi</i> <i>D. morrisiana</i> <i>D. piscatoria</i>	Yoshihira, <i>et al.</i> , 1970 Yoshihira, <i>et al.</i> , 1971b Zakaria, <i>et al.</i> , 1984 Yoshohira, <i>et al.</i> , 1970 Adeniyi <i>et al.</i> , 2000

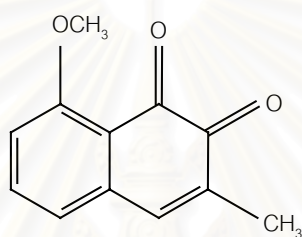
Table 1. Distribution of naphthoquinones in the genus *Diospyros* (continued)

Compounds	Sources	References
Bis-isodiospyrin (68)	<i>D. usambarensis</i>	Khan, <i>et al.</i> , 1989
6'',8'-Bisdiosquinone (69)	<i>D. mafiensis</i>	Khan and Rwekika, 1998
2.2.3 Derivatives of plumbagin and 7-methyljuglone monomers		
Ehretione (70)	<i>D. ehretioides</i>	Lillie, <i>et al.</i> , 1976b
Habinone (71)	<i>D. greeniwayi</i>	Khan and Rwekika, 1998

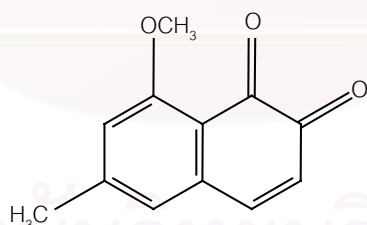
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8-Hydroxy-1,2-naphthoquinone (1)

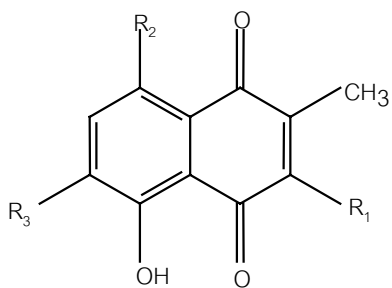


3-Methyl-8-methoxy-1,2-naphthoquinone (2)

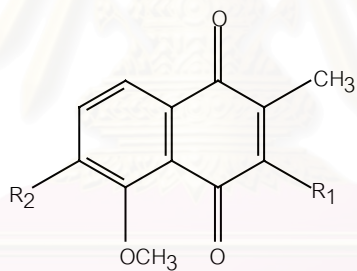


6-Methyl-8-methoxy-1,2-naphthoquinone (3)

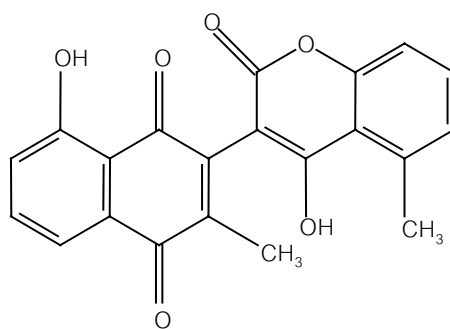
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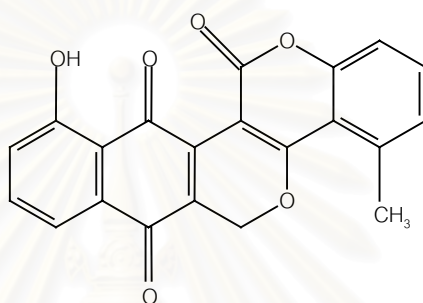
Plumbagin (4)	$R_1=R_2=R_3=H$	
3-Hydroxyplumbagin (5)	$R_1=OH$	$R_2=R_3=H$
3-Chloroplumbagin (6)	$R_1=Cl$	$R_2=R_3=H$
3-Bromoplumbagin (7)	$R_1=Br$	$R_2=R_3=H$
Methylnaphthazarin (8)	$R_1=R_3=H$	$R_2=OH$



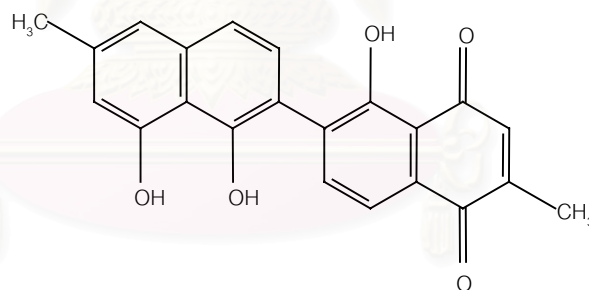
2-Methyl-5-methoxy-1,4-naphthoquinone (9)	$R_1=R_2=H$	
2-Methyl-3-hydroxy-5-methoxy-1,4-naphthoquinone (10)	$R_1=OH$	$R_2=H$
Diomelaquinone (11)	$R_1=H$	$R_2=OH$
2-Methyl-5,6-dimethoxy-1,4-naphthoquinone (12)	$R_1=H$	$R_2=OCH_3$



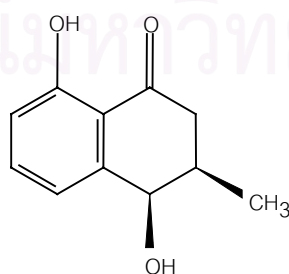
Canaliculatin (13)



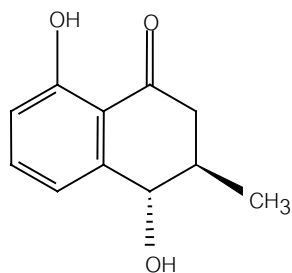
Cyclocanaliculatin (14)



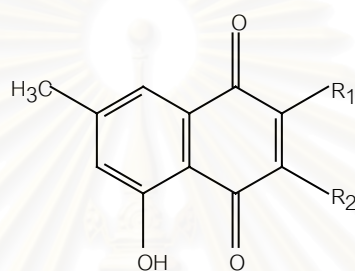
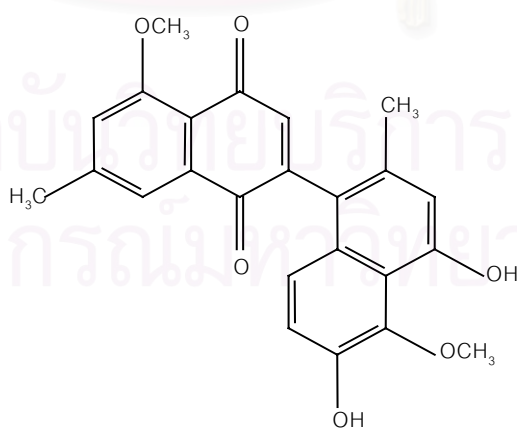
Ebenone (15)



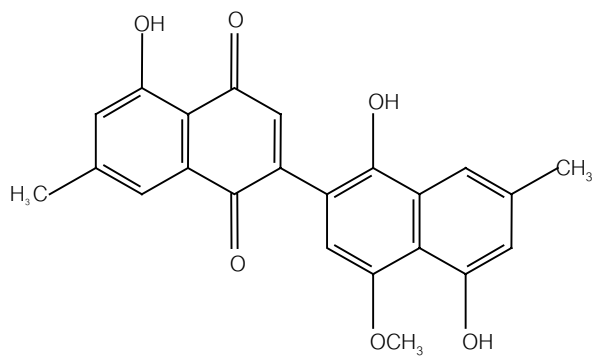
Isoshinanolone (16)



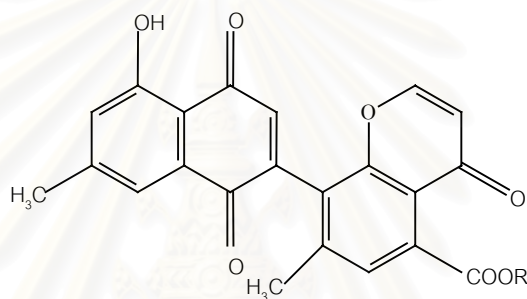
Epi-isoshinanolone (17)

7-Methyljuglone (18) $R_1=R_2=H$ 2-Methoxy-7-methyljuglone (19) $R_1=OCH_3$ $R_2=H$ 3-Methoxy-7-methyljuglone (20) $R_1=H$ $R_2=OCH_3$ 

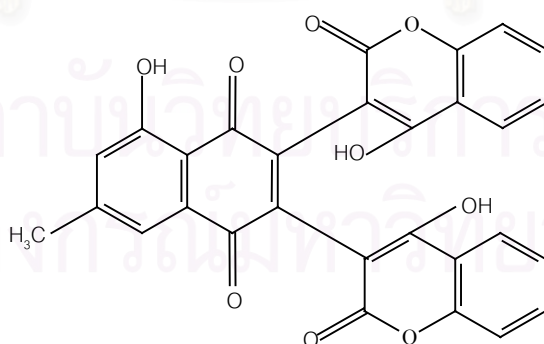
Celebaquinone (21)



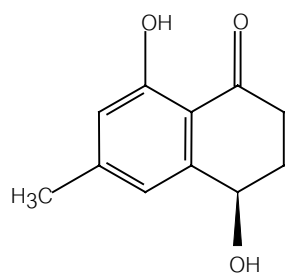
Isocelebaquinone (22)



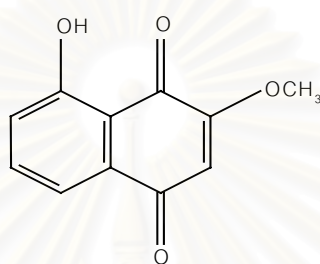
Chromenone acid (23) R= H

Chromenone ester (24) R= C₂H₅

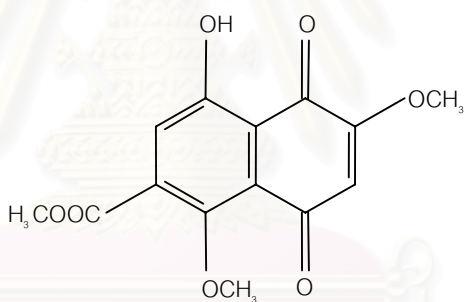
Ismailin (25)



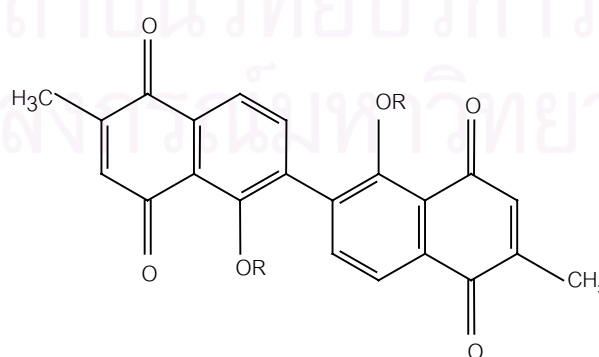
Shinanolone (26)



3-Methoxyjuglone (27)



Yerrinquinone (28)

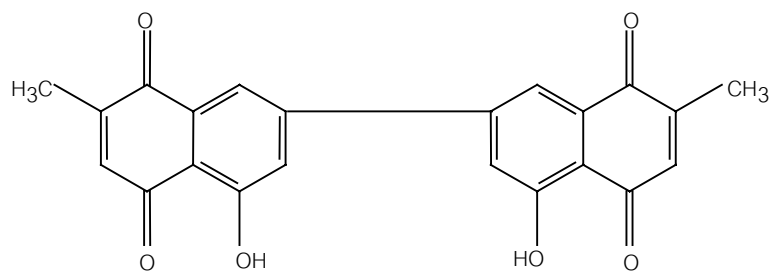


Elliptinone (29)

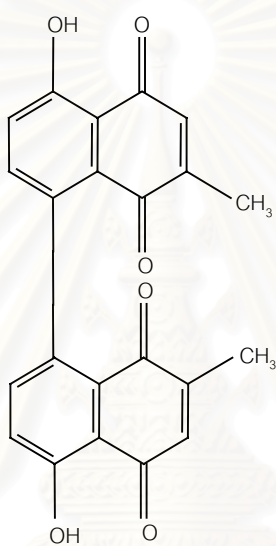
R=H

Elliptinone dimethylester (30)

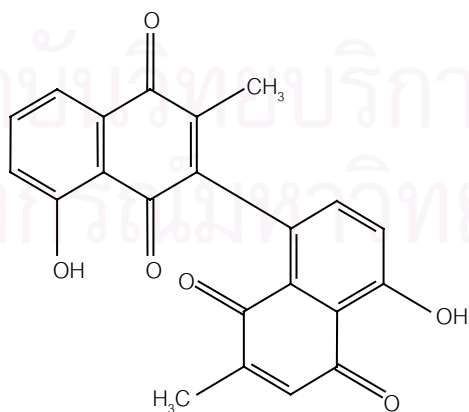
R=CH₃



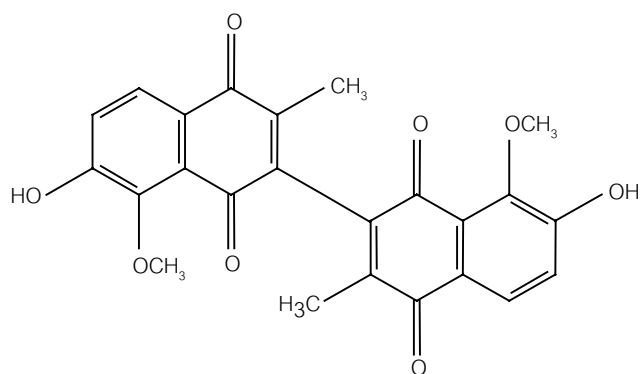
Undulatanone (31)



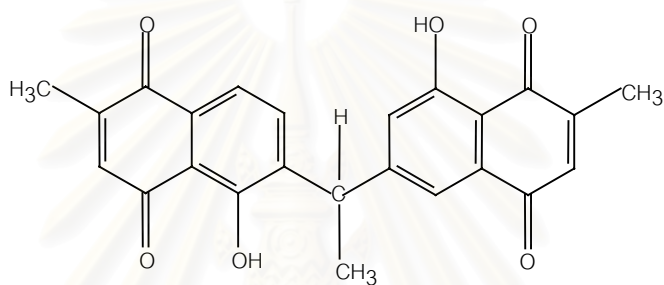
Maritinone (32)



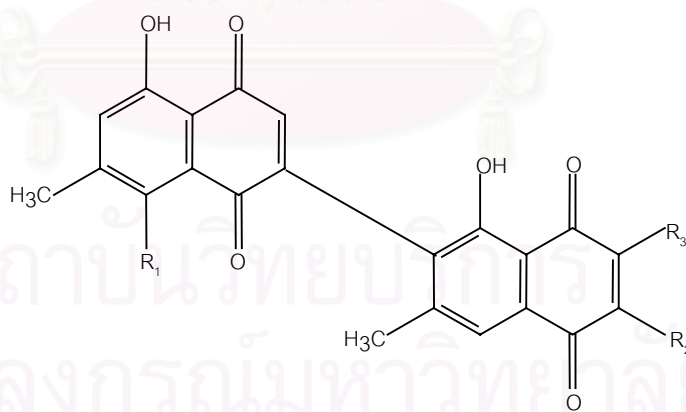
3-8'-Biplumbagin (33)



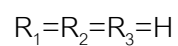
3-3'-Dimer of 6-hydroxy-5-methoxy-2-methyl-1,4-naphthoquinone (34)



Ethylidene-6,6'-biplumbagin (35)



Diospyrin (36)



8-Hydroxydiospyrin (37)



3'-Methoxydiospyrin (38)



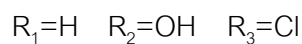
2'-Chlorodiospyrin (39)

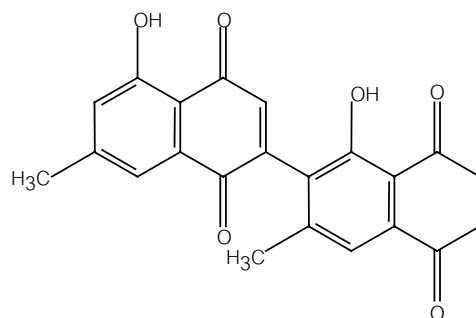


3'-Chlorodiospyrin (40)

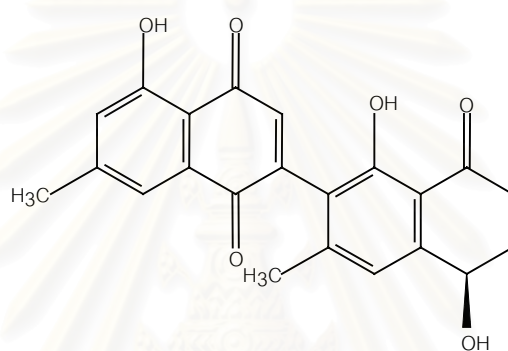


3'-Chloro-2'-hydroxydiospyrin (41)

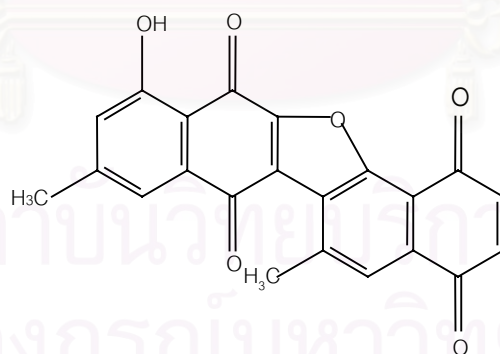




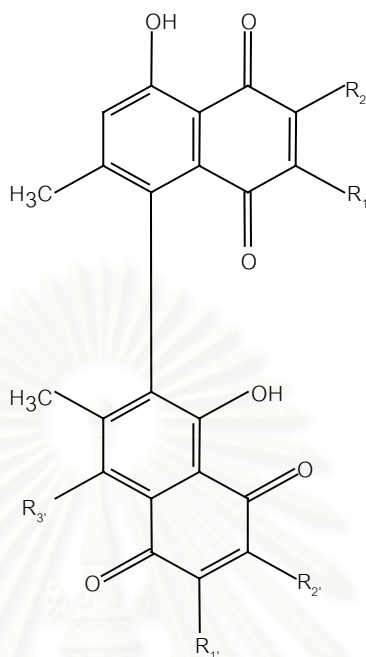
β' -Dihydrodiospyrin (42)



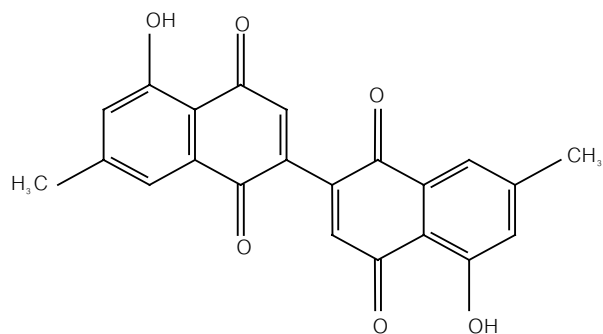
Tetrahydrodiospyrin (43)



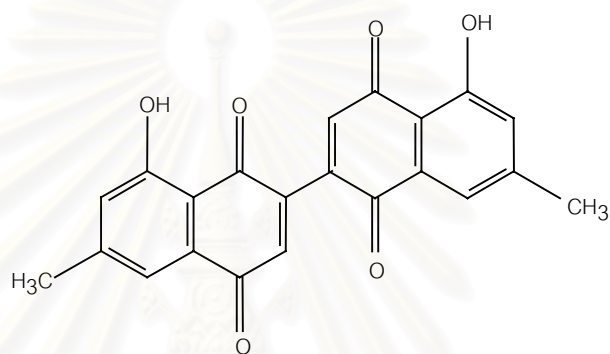
Cyclodiospyrin (44)



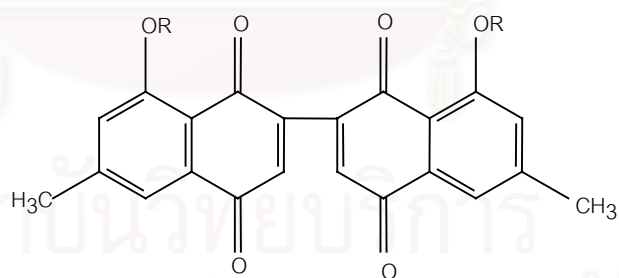
Isodiospyrin (45)	$R_1=R_2=R_{1'}=R_{2'}=R_{3'}=H$	
8'-Hydroxyisodiospyrin (46)	$R_1=R_2=R_{1'}=R_{2'}=H$	$R_{3'}=OH$
2'-Methoxyisodiospyrin (47)	$R_1=OCH_3$	$R_2=R_{1'}=R_{2'}=R_{3'}=H$
3'-Methoxyisodiospyrin (48)	$R_1=R_2=R_{1'}=R_{3'}=H$	$R_{2'}=OCH_3$
3-Ethoxyisodiospyrin (49)	$R_1=R_{1'}=R_{2'}=R_{3'}=H$	$R_2=OCH_2CH_3$
2'-Ethoxyisodiospyrin (50)	$R_1=R_2=R_{2'}=R_{3'}=H$	$R_{1'}=OCH_2CH_3$
3'-Ethoxyisodiospyrin (51)	$R_1=R_2=R_{1'}=R_{2'}=R_{3'}=H$	$R_{2'}=OCH_2CH_3$
8'-Hydroxy-3-methoxyisodiospyrin (52)	$R_1=R_{1'}=R_{2'}=H$	$R_2=OCH_3, R_{3'}=OH$
2,2'-Dimethoxyisodiospyrin (53)	$R_1=R_{1'}=OCH_3,$	$R_2=R_{2'}=R_{3'}=H$
2,3'-Dimethoxyisodiospyrin (54)	$R_1=R_{2'}=OCH_3$	$R_2=R_{1'}=R_{3'}=H$
3,3'-Dimethoxyisodiospyrin (55)	$R_1=R_{1'}=R_{3'}=H$	$R_2=R_{2'}=OCH_3,$



Biramentaceone (56)



Rotundiquinone (57)



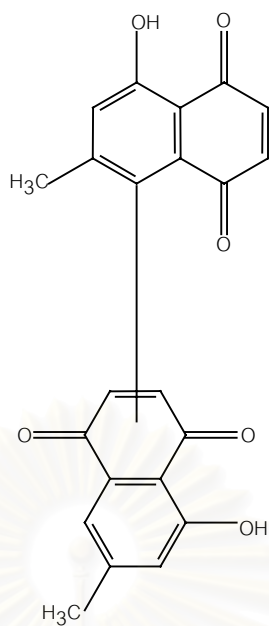
Mamegakinone (58)

R= H

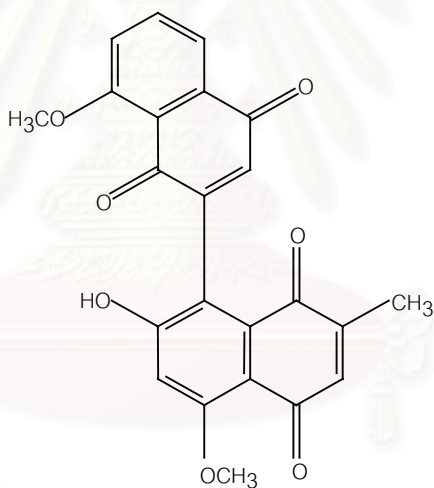
Mamegakinone dimethyl ester (59)

R= CH₃

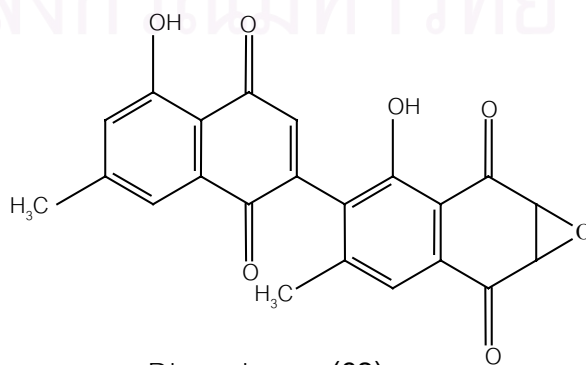
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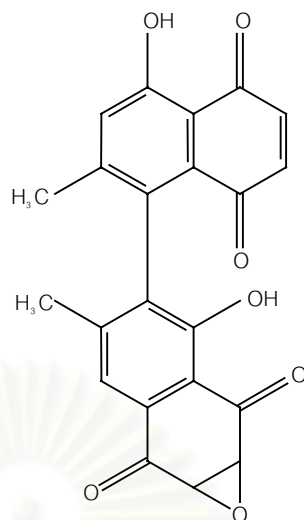
Neodiospyrin (60)



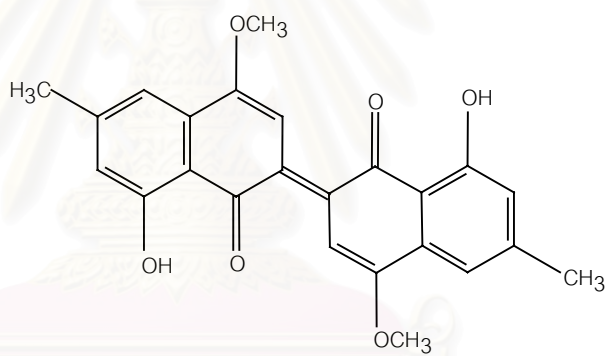
Lemuninol A (61)



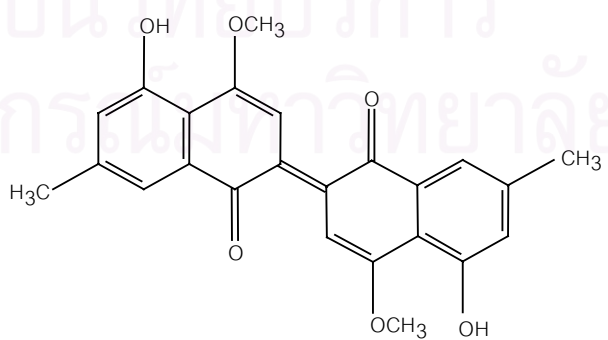
Diosquinone (62)



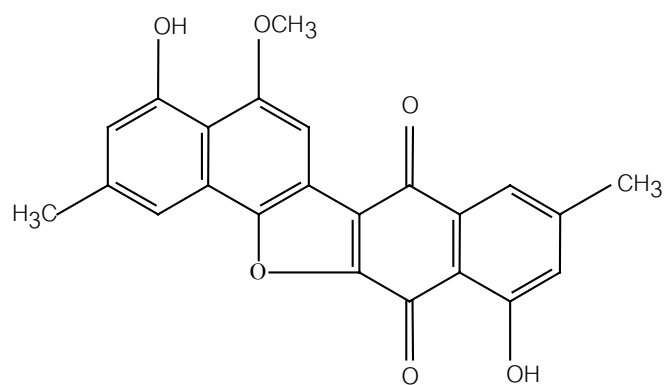
Batacanone (63)



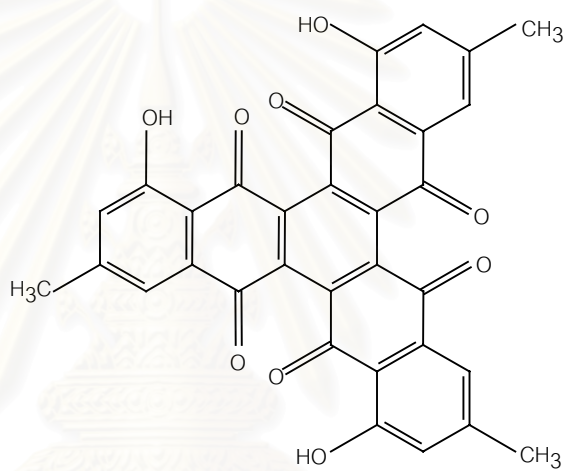
Diosindigo A (64)



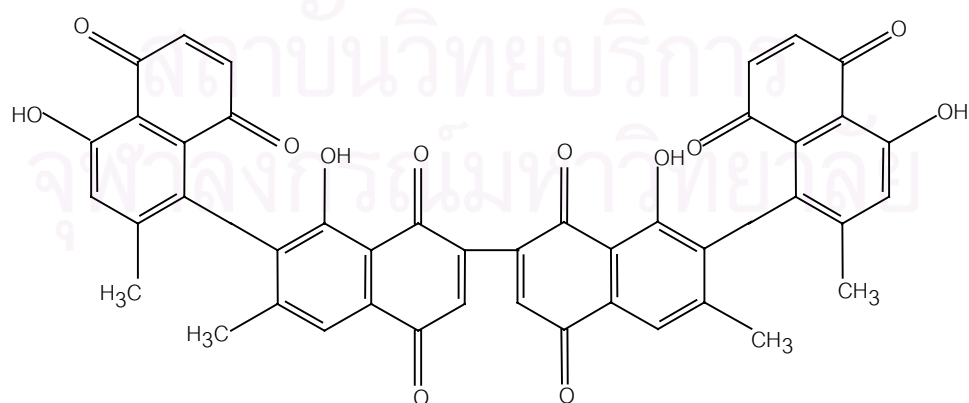
Diosindigo B (65)



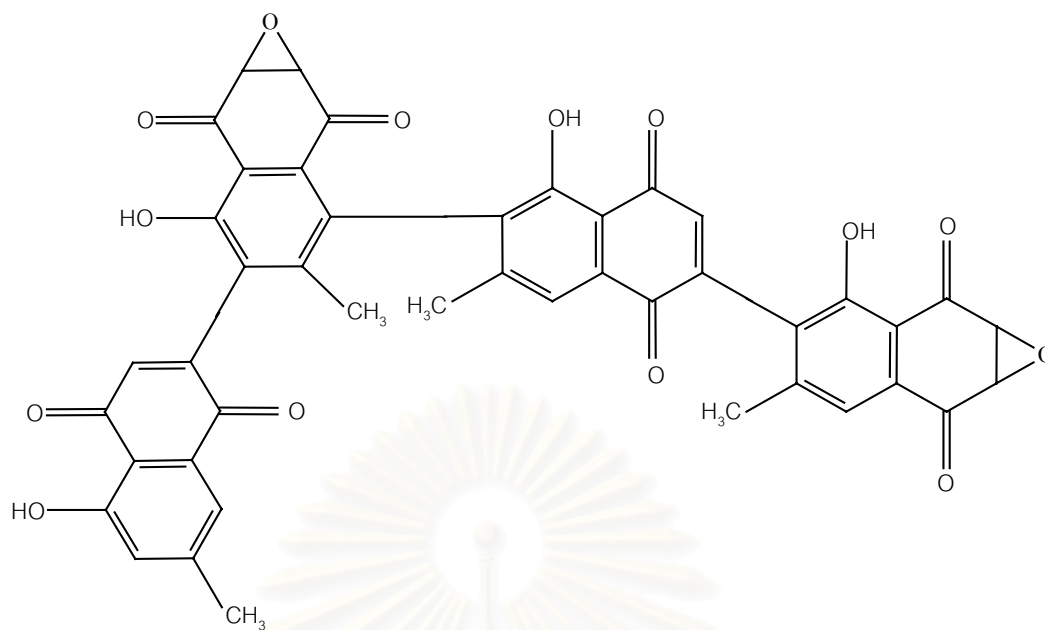
Pentacyclic quinone (66)



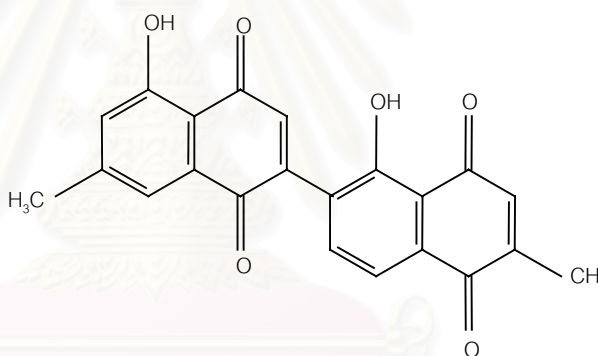
Xylospyrin (67)



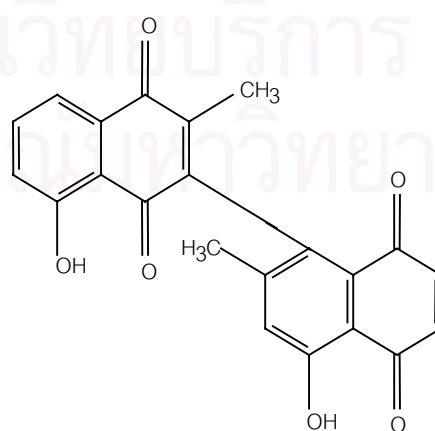
Bis-isodiospyrin (68)



6'',8''-Bisdiosquinone (69)



Ehretione (70)

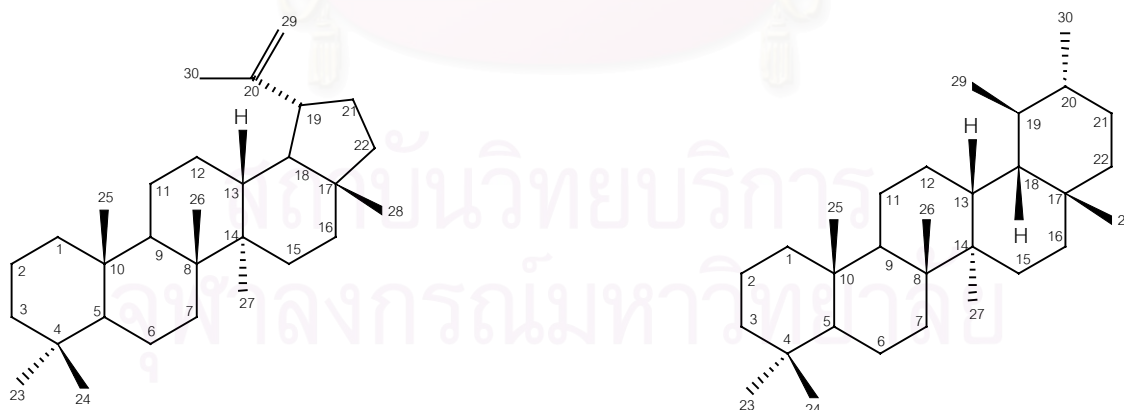


Habinone (71)

2. Triterpenoids

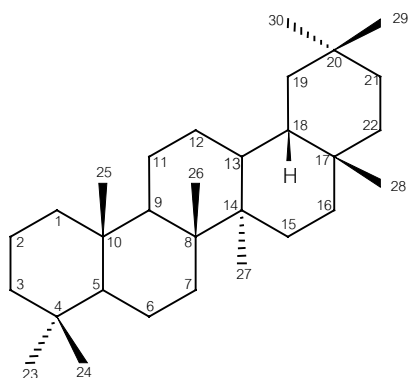
Triterpenoids are widely distributed in the genus *Diospyros*. They are found in more than 90% of *Diospyros* species screened so far and detected in almost all parts of the plants especially in the leaves and heartwood (Mallavadhani, Panda and Rao, 1998). The *Diospyros* triterpenoids isolated so far are all pentacyclic, belonging to the lupane (A), ursane (B), oleanane (C), taraxerane (D) and friedelane (E) types. Some of these compounds are found to possess interesting pharmacological activities such as anti-tumor [betulinic acid (Yan, *et al*, 1989), lupeol (Kuo, *et al*, 1997c)] and anti-inflammatory activities [betulin, betulinic acid and ursolic acid (Recio, *et al*, 1995)].

Of the five triterpene skeletal types found in *Diospyros*, the lupane skeleton is the most common. Major compounds of this type are lupeol, betulin and betulinic acid. Two other classes of triterpenoids which are prevalent in *Diospyros* are the ursanes and the oleananes. α -Amyrin, ursolic acid and baurenol are major compounds of the ursane type while β -amyrin and oleanolic acid are of the oleanane type. For the last two skeletal types only 3 taraxeranes and 4 friedelanes have so far been isolated from *Diospyros* species.

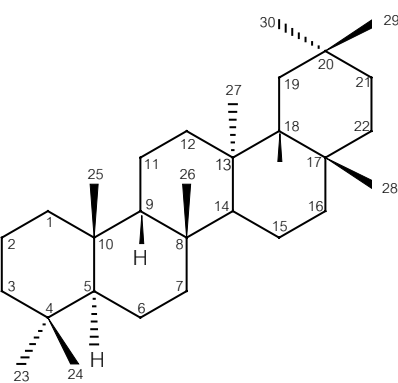


Lupane (A)

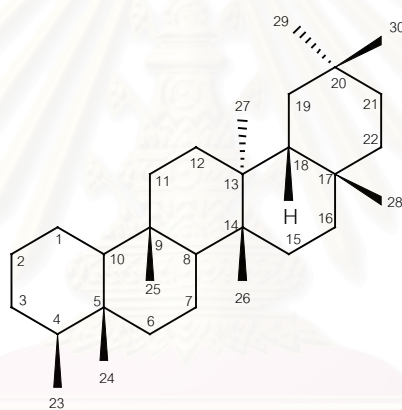
Ursane (B)



Oleanane (C)



Taraxerane (D)



Friedelane (E)

The distribution of triterpenoids within the genus *Diospyros* is summarized in Table 2.

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Table 2. Distribution of triterpenoids in the genus *Diospyros*

Compounds	Sources	References
<p>1. Lupane type</p> <p>Lupeol (72)</p>	<p><i>D. abyssinica</i></p> <p><i>D. acuta</i></p> <p><i>D. argentea</i></p> <p><i>D. bipidensis</i></p> <p><i>D. buxifolia</i></p> <p><i>D. canaliculata</i></p> <p><i>D. candolleana</i></p> <p><i>D. castanea</i></p> <p><i>D. cauliflora</i></p> <p><i>D. chevalieri</i></p> <p><i>D. cinnabarina</i></p> <p><i>D. consulatae</i></p> <p><i>D. cordifolia</i></p> <p><i>D. cornii</i></p>	<p>Zhong, <i>et al.</i>,1984</p> <p>Herath, <i>et al.</i> 1978</p> <p>Zakaria, <i>et al.</i>, 1984</p> <p>Waterman and Mbi, 1979</p> <p>Bhakuni, <i>et al.</i>, 1971</p> <p>Zhong, <i>et al.</i>,1984</p> <p>Desai, <i>et al.</i>, 1970</p> <p>Musgrave and Skoyles , 1974</p> <p>Musgrave and Skoyles , 1974</p> <p>Zhong, <i>et al.</i>,1984</p> <p>Waterman and Mbi, 1979 ; Zhong, <i>et al.</i>,1984</p> <p>Khan, <i>et al.</i>, 1987</p> <p>Chandra and Shastry, 1989</p> <p>Khan, Nkunya and Wevers, 1980</p>

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Lupeol (72)	<i>D. crassiflora</i>	Zhong, <i>et al.</i> , 1984
	<i>D. curranii</i>	Musgrave and Skoyles, 1974
	<i>D. dendo</i>	Zhong, <i>et al.</i> , 1984
	<i>D. dipenhorstii</i>	Musgrave and Skoyles, 1974
	<i>D. discolor</i>	Zakaria, <i>et al.</i> , 1984
	<i>D. ebenum</i>	Gupta and Mahadevan, 1967; Gupta and Mahadevan, 1968
	<i>D. ehretioides</i>	Musgrave and Skoyles, 1974
	<i>D. elliptifolia</i>	Musgrave, <i>et al.</i> , 1974
	<i>D. embryopteris</i>	Bhakuni, <i>et al.</i> , 1971
	<i>D. eriantha</i>	Chen, <i>et al.</i> , 1994
	<i>D. evena</i>	Musgrave, <i>et al.</i> , 1974
	<i>D. exsculpta</i>	Bhakuni, <i>et al.</i> , 1971
	<i>D. fragrans</i>	Zhong, <i>et al.</i> , 1984
	<i>D. gabunensis</i>	Zhong, <i>et al.</i> , 1984

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Lupeol (72)	<i>D. gracilescens</i>	Wareman and Mbi, 1979 ; Zhong, <i>et al.</i> ,1984
	<i>D. greeniwayi</i>	Khan and Rwekika, 1998
	<i>D. guianensis</i>	Braneton and Moretti, 1979
	<i>D. hallierii</i>	Khan and Timi, 1999a
	<i>D. hirsuta</i>	Herath, <i>et al.</i> , 1978
	<i>D. hoyleana</i>	Zhong, <i>et al.</i> ,1984
	<i>D. ismailii</i>	Zakaria, <i>et al.</i> , 1984
	<i>D. iturensis</i>	Zhong, <i>et al.</i> ,1984
	<i>D. kaki</i>	Tezuka, <i>et al.</i> , 1972; Lin <i>et al.</i> , 1988
	<i>D. kaki</i> var. <i>sylvestris</i>	Tezuka, <i>et al.</i> , 1972
	<i>D. kamerunensis</i>	Zhong, <i>et al.</i> ,1984
	<i>D. kirkii</i>	Maria, <i>et al.</i> , 1979
	<i>D. longiflora</i>	Zhong, <i>et al.</i> ,1984
	<i>D. lotus</i>	Yoshihira, <i>et al.</i> , 1971b ; Zakaria, <i>et al.</i> , 1984
<i>D. mafiensis</i>	Khan and Rwekika, 1992	

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Lupeol (72)	<i>D. maingayi</i> <i>D. mannii</i> <i>D. maritima</i> <i>D. melanoxylon</i> <i>D. mespiliformis</i> <i>D. microphylla</i> <i>D. mollis</i> <i>D. monobuttensis</i> <i>D. montana</i> <i>D. moonii</i> <i>D. morrisiana</i> <i>D. natalensis</i> <i>D. obliquifolia</i>	Musgrave and Skoyles , 1974 ; Zakaria, <i>et al.</i> , 1984 Jeffreys, <i>et al.</i> , 1983 Tezuka, <i>et al.</i> , 1973 Sankaram and Sidhu, 1964; Gupta and Roa, 1964 Zhong, <i>et al.</i> ,1984 Bhakuni, <i>et al.</i> , 1971 Yoshihira, <i>et al.</i> , 1971a ; Musgrave and Skoyles, 1974 Zhong, <i>et al.</i> ,1984 Musgrave and Skoyles , 1974 ; Narayan, Row and Satyanarayana, 1978 ; Kapil and Dhar, 1961 Herath, <i>et al.</i> , 1978 Yoshihira, <i>et al.</i> , 1971b Khan and Rwekika, 1992 Waterman amd Mbi, 1979

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Lupeol (72)	<i>D. oblongifolia</i>	Herath, <i>et al.</i> , 1978
	<i>D. oppositifolia</i>	Herath, <i>et al.</i> , 1978
	<i>D. peregrina</i>	Bhaumik, <i>et al.</i> , 1971 ; Mirsa, <i>et al.</i> , 1971
	<i>D. pseudo-malabarica</i>	Musgrave and Skoyles, 1974
	<i>D. quaesita</i>	Herath, <i>et al.</i> , 1978
	<i>D. rheophytica</i>	Herath, <i>et al.</i> , 1978
	<i>D. rhodocalyx</i>	Musgrave and Skoyles, 1974
	<i>D. rotundifolia</i>	Gupta and Roa, 1964
	<i>D. sanza-minika</i>	Musgrave and Skoyles , 1974 ; Zhong, <i>et al.</i> ,1984
	<i>D. siamang</i>	Zakaria,, <i>et al.</i> , 1984
	<i>D. siamensis</i>	Musgrave and Skoyles , 1974
	<i>D. siderophylla</i>	Li, <i>et al.</i> ,1982
	<i>D. singaporensis</i>	Zakaria, <i>et al.</i> , 1984
	<i>D. spinescens</i>	Herath, <i>et al.</i> , 1978
<i>D. sumatrana</i>	Zakaria, <i>et al.</i> , 1984	

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Lupeol (72)	<i>D. sylvatica</i> <i>D. thwaitesii</i> <i>D. tomentosa</i> <i>D. toposia</i> <i>D. undulata</i> var. <i>cratericalyx</i> <i>D. villosiuscula</i> <i>D. variegata</i> <i>D. virginiana</i> <i>D. walkeri</i> <i>D. wallichii</i> <i>D. zenkeri</i>	Rao, <i>et al.</i> , 1966; Gupta and Roa, 1964 Herath, <i>et al.</i> , 1978 Bhakani, <i>et al.</i> , 1971 Musgrave and Skoyles, 1974 Aoonpakh, 2001 Khan and Timi, 1999c Musgrave and Skoyles, 1974 Shukla and Kapadia, 1989 Herath, <i>et al.</i> , 1984 Zakaria, <i>et al.</i> , 1984 Zhong, <i>et al.</i> , 1984
Epi-lupeol (73)	<i>D. ebenaster</i> <i>D. palmeri</i>	Dominguez, <i>et al.</i> , 1979 Dominguez, <i>et al.</i> , 1979

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Lupenone (74)	<i>D. mollis</i>	Yoshihira, <i>et al.</i> , 1971a
Betulin (75)	<i>D. abyssinica</i>	Zhong, <i>et al.</i> , 1984
	<i>D. argentea</i>	Zakaria, <i>et al.</i> , 1984
	<i>D. bipidensis</i>	Waterman and Mbi, 1979
	<i>D. buxifolia</i>	Bhakuni, <i>et al.</i> , 1971
	<i>D. canaliculata</i>	Zhong, <i>et al.</i> , 1984
	<i>D. candolleana</i>	Desai, <i>et al.</i> , 1970
	<i>D. castanea</i>	Musgrave and Skoyles, 1974
	<i>D. cauliflora</i>	Musgrave and Skoyles, 1974
	<i>D. chevalieri</i>	Zhong, <i>et al.</i> , 1984
	<i>D. chloroxylon</i>	Matsura, <i>et al.</i> , 1971
	<i>D. cinnabarina</i>	Waterman and Mbi, 1979 ; Zhong, <i>et al.</i> , 1984
	<i>D. consolatae</i>	Khan, <i>et al.</i> , 1987
	<i>D. cornii</i>	Khan, Nkunya and Wevers, 1980

Table2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Betulin (75)	<i>D. crassiflora</i> <i>D. curranii</i> <i>D. dendo</i> <i>D. diepenhorstii</i> <i>D. discolor</i> <i>D. ebenaster</i> <i>D. ebenum</i> <i>D. elliptifolia</i> <i>D. embryopteris</i> <i>D. eriantha</i> <i>D. evena</i> <i>D. exsculpta</i> <i>D. fragrans</i> <i>D. gabunensis</i>	Zhong, <i>et al.</i> ,1984 Musgrave and Skoyles , 1974 Zhong, <i>et al.</i> ,1984 Balza, <i>et al.</i> , 1989 Zakaria, <i>et al.</i> , 1984 Dominguez , <i>et al.</i> , 1979 Gupta and Mahadevan, 1967; Gupta and Mahadevan, 1968 Musgrave <i>et al.</i> , 1974 Bhakuni, <i>et al.</i> , 1971 Chen, <i>et al.</i> , 1994 Musgrave and Skoyles , 1974 Bhakuni, <i>et al.</i> , 1971 Zhong, <i>et al.</i> ,1984 Zhong, <i>et al.</i> ,1984

Table2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Betulin (75)	<i>D. guianensis</i> <i>D. gracilescens</i> <i>D. guianensis</i> <i>D. hirsuta</i> <i>D. hoyleana</i> <i>D. indica</i> <i>D. ismailii</i> <i>D. iturensis</i> <i>D. kaki</i> <i>D. kaki var. sylvestris</i> <i>D. kamerunensis</i> <i>D. kirkii</i> <i>D. leucomelas</i> <i>D. longiflora</i>	Zhong, <i>et al.</i> ,1984 Waterman and Mbi, 1979 ; Zhong <i>et al.</i> ,1984 Braneton and Moretii, 1979 Herath,, <i>et al.</i> , 1978 Zhong, <i>et al.</i> ,1984 Hayek , <i>et al.</i> , 1989 Zakaria,, <i>et al.</i> , 1984 Zhong, <i>et al.</i> ,1984 Matsura <i>et al.</i> , 1971 ; Andriamasy and Fouraste, 1978 Tezuka, <i>et al.</i> , 1972 Zhong, <i>et al.</i> ,1984 Maria, <i>et al.</i> , 1979 Recio, <i>et al.</i> , 1995 Zhong, <i>et al.</i> ,1984

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Betulin (75)	<i>D. lotus</i> <i>D. maingayi</i> <i>D. malanonilau</i> <i>D. mannii</i> <i>D. maritima</i> <i>D. melanoxylon</i> <i>D. mespiliformis</i> <i>D. microphyla</i> <i>D. mollis</i> <i>D. monobuttensis</i> <i>D. montana</i> <i>D. moonii</i> <i>D. morrisiana</i>	Yoshihira, <i>et al.</i> , 1971b ; Zakaria, <i>et al.</i> , 1984 Musgrave and Skoyles, 1974; Zakaria, <i>et al.</i> , 1984 Singh and Prakask, 1988 Jeffreys, <i>et al.</i> , 1983 Tezuka, <i>et al.</i> , 1973 Sankaram and Sidhu, 1964; Gupta and Roa, 1964 Zhong, <i>et al.</i> , 1984 Bhakuni, <i>et al.</i> , 1971 Yoshihira, <i>et al.</i> , 1971a ; Musgrave and Skoyles, 1974 Zhong, <i>et al.</i> , 1984 Musgrave and Skoyles , 1974 ; Narayan, <i>et al.</i> , 1978 Herath, <i>et al.</i> , 1978 Yoshihira, <i>et al.</i> , 1971b

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Betulin (75)	<i>D. obliquifolia</i> <i>D. oblongifolia</i> <i>D. peregrina</i> <i>D. pseudo-malabarica</i> <i>D. quaesita</i> <i>D. rhodocalyx</i> <i>D. rotundifolia</i> <i>D. sanza-minika</i> <i>D. siamang</i> <i>D. siamensis</i> <i>D. siderophylla</i> <i>D. singaporensis</i> <i>D. spinescens</i> <i>D. sumatrana</i> <i>D. sylvatica</i>	Waterman and Mbi, 1979 Herath, <i>et al.</i> , 1978 Bhakuni, <i>et al.</i> , 1971 ; Mirsa, <i>et al.</i> , 1971 Musgrave and Skoyles , 1974 Herath, <i>et al.</i> , 1978 Musgrave and Skoyles , 1974 Gupta and Roa, 1964 Musgrave and Skoyles , 1974 ; Zhong, <i>et al.</i> ,1984 Zakaria, <i>et al.</i> , 1974 Musgrave and Skoyles , 1974 Li, <i>et al.</i> ,1981 Zakaria, <i>et al.</i> , 1984 Herath, <i>et al.</i> , 1984 Zakaria, <i>et al.</i> , 1984 Rao, <i>et al.</i> , 1966; Gupta and Roa, 1964

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Betulin (75)	<i>D. thwaitesii</i> <i>D. tomentosa</i> <i>D. undulata</i> var. <i>cratericalyx</i> <i>D. variegata</i> <i>D. verrucosa</i> <i>D. virainiana</i> <i>D. walkeri</i> <i>D. wallichii</i> <i>D. zenkeri</i>	Herath, <i>et al.</i> , 1984 Bhakani, <i>et al.</i> , 1971 Aoonpakh, 2001 Musgrave and Skoylas, 1974 Khan, Kishimba and Locksley, 1987 Hayek, <i>et al.</i> , 1989 Herath, <i>et al.</i> , 1984 Zakaria, <i>et al.</i> , 1984 Zhong, <i>et al.</i> , 1984

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Betulinic acid (76)	<i>D. abyssinica</i> <i>D. alboflavescens</i> <i>D. argentea</i> <i>D. bipidensis</i> <i>D. buxifolia</i> <i>D. canaliculata</i> <i>D. candolleana</i> <i>D. castanea</i> <i>D. cauliflora</i> <i>D. chevalieri</i> <i>D. chloroxylon</i> <i>D. cinnabarina</i> <i>D. consolatae</i> <i>D. crassiflora</i> <i>D. curranii</i>	Zhong, <i>et al.</i> ,1984 Bouquet, 1972 Zakaria, <i>et al.</i> , 1984 Waterman and Mbi, 1979 Bhakuni, <i>et al.</i> , 1971 Zhong, <i>et al.</i> ,1984 Desai, <i>et al.</i> , 1970 Musgrave and Skoyles, 1974 Musgrave and Skoyles, 1974 Zhong, <i>et al.</i> ,1984; Hayek <i>et al.</i> , 1989 Matura, <i>et al.</i> ,1971 Waterman and Mbi, 1979 ; Zhong, <i>et al.</i> ,1984 Khan, <i>et al.</i> , 1980 Zhong, <i>et al.</i> ,1984 Musgrave and Skoyles , 1974

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Betulinic acid (76)	<i>D. dendo</i> <i>D. dipenhorstii</i> <i>D. discolor</i> <i>D. ebenum</i> <i>D. ehretioides</i> <i>D. elliptifolia</i> <i>D. embryopteris</i> <i>D. eriantha</i> <i>D. evena</i> <i>D. exsculpta</i> <i>D. ferrea</i> <i>D. fragrans</i> <i>D. gabunensis</i> <i>D. gilleti</i> <i>D. gracilescens</i>	Zhong, <i>et al.</i> ,1984 Musgrave and Skoyles , 1974 Lin, 1978 ; Zakaria, <i>et al.</i> , 1984 Brown and Thomson, 1965 Musgrave and Skoyles, 1974 Musgrave <i>et al.</i> , 1974 Bhakun, <i>et al.</i> , 1971 Chen, <i>et al.</i> , 1994 Musgrave, <i>et al.</i> , 1974 Bhakuni, <i>et al.</i> , 1971 Bhakuni, <i>et al.</i> , 1971 Zhong, <i>et al.</i> ,1984 Zhong, <i>et al.</i> ,1984 Bouquet, 1973 Wareman and Mbi, 1979 ; Zhong <i>et al.</i> ,1984

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Betulinic acid (76)	<i>D. greeniwayi</i> <i>D. guianensis</i> <i>D. hirsuta</i> <i>D. hoyleana</i> <i>D. ismailii</i> <i>D. iturensis</i> <i>D. kaki</i> <i>D. kaki</i> var. <i>sylvestris</i> <i>D. kamerunensis</i> <i>D. leucomelas</i> <i>D. longiflora</i> <i>D. lotus</i> <i>D. mafiensis</i> <i>D. maingayi</i>	Khan and Rwekika, 1998 Braneton and Moretti, 1979 Herath, <i>et al.</i> , 1978 Zhong, <i>et al.</i> , 1984 Zakaria, <i>et al.</i> , 1984 Zhong, <i>et al.</i> , 1984 Tezuka, <i>et al.</i> , 1972; Lin <i>et al.</i> , 1988 Tezuka, <i>et al.</i> , 1972 Zhong, <i>et al.</i> , 1984 Recio, <i>et al.</i> , 1995 Zhong, <i>et al.</i> , 1984 Yoshihira <i>et al.</i> , 1971b ; Zakaria, <i>et al.</i> , 1984 Khan and Rwekika, 1999 Musgrave and Skoyles , 1974 ; Zakaria, <i>et al.</i> , 1984

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Betulinic acid (76)	<i>D. mannii</i> <i>D. maritima</i> <i>D. mespiliformis</i> <i>D. melanoxylon</i> <i>D. monobuttensis</i> <i>D. montana</i> <i>D. moonii</i> <i>D. morrisiana</i> <i>D. natalensis</i> <i>D. obliquifolia</i> <i>D. palmeri</i> <i>D. peregrina</i> <i>D. pseudo-malabarica</i> <i>D. quaesita</i>	Jeffreys <i>et al.</i> , 1983 Tezuka, <i>et al.</i> , 1973 Zhong, <i>et al.</i> , 1984 Sankaram and Sidhu, 1964; Gupta and Roa, 1964 Zhong, <i>et al.</i> , 1984 Musgrave and Skoyles , 1974 ; Narayan, <i>et al.</i> , 1978 Herath, <i>et al.</i> , 1978 Yoshihira, <i>et al.</i> , 1971b Khan and Rwekika, 1992 Waterman amd Mbi, 1979 Dominguez, <i>et al.</i> , 1979 Bhaumik, <i>et al.</i> , 1971 Musgrave and Skoyles , 1974 Herath,, <i>et al.</i> , 1978

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Betulinic acid (76)	<i>D. sanza-minika</i> <i>D. siamang</i> <i>D. siamensis</i> <i>D. siderophylla</i> <i>D. singaporensis</i> <i>D. spinescens</i> <i>D. sumatrana</i> <i>D. sylvatica</i> <i>D. thwaitesii</i> <i>D. tomentosa</i> <i>D. verrucosa</i> <i>D. virginiana</i> <i>D. walkeri</i> <i>D. wallichii</i>	Musgrave and Skoyles , 1974 ; Zhong, <i>et al.</i> ,1984 Zakaria, <i>et al.</i> , 1974 Musgrave and Skoyles , 1974 Li, <i>et al.</i> ,1982 Zakaria, <i>et al.</i> , 1984 Herath, <i>et al.</i> , 1984 Zakaria, <i>et al.</i> , 1984 Rao, <i>et al.</i> , 1966 ; Gupta and Roa, 1964 Herath, <i>et al.</i> , 1984 Bhakani, <i>et al.</i> , 1971 Khan, Nkunya and Wevers, 1980 ; Khan <i>et al.</i> , 1987a Skukla and Kapadia, 1989 Herath, <i>et al.</i> , 1984 Zakaria, <i>et al.</i> , 1984

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Betulinic acid (76)	<i>D. zenkeri</i>	Zhong, <i>et al.</i> ,1984
Betulinaldehyde (77)	<i>D. canaliculata</i> <i>D. eriantha</i>	Zhong, <i>et al.</i> ,1984 Chen, <i>et al.</i> , 1992
Peregrinol (78)	<i>D. peregrina</i>	Jain and Yadav, 1994
3-(Z)-Coumaroyllupeol (79)	<i>D. maritima</i>	Chang and Kuo, 1999
3-(E)-Coumaroyl-28-palmitoylbetulin (80)	<i>D. maritima</i>	Chang and Kuo, 1998
3-(Z)-Coumaroyl-28-palmitoylbetulin (81)	<i>D. maritima</i>	Chang and Kuo, 1998
3-(E)-Feruloylbetulin (82)	<i>D. maritima</i>	Kuo, Chang and Kuo, 1997b

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
3-(<i>E</i>)-Feruloyl-28-palmitoylbetulin (83)	<i>D. maritima</i>	Chang and Kuo, 1998
3-(<i>E</i>)-Coumaroylbetulinaldehyde (84)	<i>D. maritima</i>	Chang and Kuo, 1999
3-(<i>E</i>)-Coumaroylbetulin-28-yl ethylnonanedioate (85)	<i>D. maritima</i>	Kuo and Chang , 2000
3-(<i>E</i>)-Coumaroylbetulin-28-yl ethylsuccinate (86)	<i>D. maritima</i>	Kuo and Chang , 2000
3-(<i>E</i>)-Coumaroylbetulin-28-yl ethyl (2 <i>R</i>)-2-hydroxysuccinate (87)	<i>D. maritima</i>	Kuo and Chang , 2000
28-Acetyl-3-(<i>E</i>)-coumaroylbetulin (88)	<i>D. maritima</i>	Kuo, Chang and Kuo, 1997b

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Diospyrolide (89)	<i>D. maritima</i>	Kuo, Chang and Kuo, 1997a
2. Ursane type α -Amyrin (90)	<i>D. cordifolia</i> <i>D. cornii</i> <i>D. ebenum</i> <i>D. kaki</i> <i>D. kirkii</i> <i>D. mafiensis</i> <i>D. maingayi</i> <i>D. melanoxylon</i> <i>D. mespilliformis</i> <i>D. montana</i> <i>D. natalensis</i>	Chandra and Shastry, 1989 Gafner, <i>et al.</i> , 1987; Khan, <i>et al.</i> , 1979 Brown and Thomson, 1965; Gupta and Mahadevan, 1967 Braza, <i>et al.</i> , 1989 Khan, <i>et al.</i> , 1980; Khan, <i>et al.</i> , 1979 Khan and Rwekika, 1992 Zakaria, <i>et al.</i> , 1984 Choudhary, 1973 Khan, <i>et al.</i> , 1980; Khan, <i>et al.</i> , 1979 Misra, Nigam and Mitra, 1972 Khan and Rwekika, 1992

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
α -Amyrin (90)	<i>D. sylvatica</i>	Rao, <i>et al.</i> , 1966 ; Gupta and Roa, 1964
α -Amyrone (91)	<i>D. ebenum</i>	Sharma and Gupta., 1985; Gupta and Mahadevan, 1981
Ursolic acid (92)	<i>D. castanea</i>	Musgrave and Skoyles, 1974
	<i>D. cauliflora</i>	Musgrave and Skoyles, 1974
	<i>D. cordifolia</i>	Chandra and Shastry, 1989
	<i>D. curranii</i>	Musgrave and Skoyles, 1974
	<i>D. ebenum</i>	Gupta and Mahadevan, 1968
	<i>D. evena</i>	Musgrave and Skoyles, 1974
	<i>D. ferea</i>	Bhakuni <i>et al.</i> , 1971
	<i>D. hirsuta</i>	Herath, <i>et al.</i> , 1978
<i>D. kaki</i>	Matsura <i>et al.</i> , 1971; Matsura and linuma, 1977	
<i>D. leucomelas</i>	Recio <i>et al.</i> , 1995	

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Ursolic acid (92)	<i>D. lotus</i> <i>D. malanonilau</i> <i>D. melanoxyton</i> <i>D. montana</i> <i>D. morrisiana</i> <i>D. quaesita</i> <i>D. tomentosa</i>	Yoshihira, <i>et al.</i> , 1971b ; Zakaria, <i>et al.</i> , 1984 Singh and Prakash, 1988 Sankaram and Sidhu, 1964 Musgrave and Skoyles, 1974; Mirsa, <i>et al.</i> , 1972 Yoshihira, <i>et al.</i> , 1971 Herath, <i>et al.</i> , 1978 Bhakuni <i>et al.</i> , 1971
Ursolic acid acetate (93)	<i>D. eriantha</i> <i>D. lotus</i>	Chen, <i>et al.</i> , 1992 Yoshihira, <i>et al.</i> , 1970; Hasan, <i>et al.</i> , 1975
Ursolic acid palmitate (94)	<i>D. montana</i>	Misra, <i>et al.</i> , 1972
Ursolic acid stearate (95)	<i>D. montana</i>	Misra, <i>et al.</i> , 1972

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Uvaol (96)	<i>D. kaki</i> <i>D. lotus</i> <i>D. maingayi</i> <i>D. melanoxylon</i>	Lin, <i>et al.</i> , 1988 Zakaria, <i>et al.</i> , 1984 Zakaria, <i>et al.</i> , 1984 Mallavadhani, Panda and Rao, 2001
Epi-uvaol (97)	<i>D. montana</i>	Dutta, Dutta ant Chakravarti, 1972
Bauerenol (98)	<i>D. ebenum</i> <i>D. kirkii</i> <i>D. melanoxylon</i> <i>D. mespoliformis</i> <i>D. sylvatica</i>	Gupta and Mahadevan, 1967 Khan, <i>et al.</i> , 1979; Khan, <i>et al.</i> , 1987 Mallavadhani, <i>et al.</i> , 1998 Khan, <i>et al.</i> , 1979; Khan, <i>et al.</i> , 1987 Mallavadhani, <i>et al.</i> , 1998
Corsolic acid (99)	<i>D. melanoxylon</i>	Mallavadhani, <i>et al.</i> , 2001

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
19 α -Hydroxyursolic acid (100)	<i>D. kaki</i>	Matsura and linuma, 1977
Pomolic acid methyl ester (101)	<i>D. melanoxylon</i>	Mallavadhani, <i>et al</i> , 2001
Marsformosanone (102)	<i>D. peregrina</i>	Bhaumik <i>et al.</i> , 1981
3 β -Acetoxy-urs-11-ene-28,13-olide (103)	<i>D. eriantha</i>	Chen <i>et al.</i> , 1992
3. Oleanane type		
β -Amyrin (104)	<i>D. cordifolia</i>	Chandra and Shastry, 1989
	<i>D. lotus</i>	Yoshihira, <i>et al.</i> , 1971; Hasan, <i>et al.</i> , 1975
	<i>D. melanoxylon</i>	Mallavadhani, <i>et al.</i> , 2001
	<i>D. morrisiana</i>	Yan <i>et al.</i> , 1989
	<i>D. perigrina</i>	Tandon, Tiwari and Varshney, 1974

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Oleanolic acid (105)	<i>D. cauliflora</i>	Musgrave and Skoyles , 1974
	<i>D. castania</i>	Musgrave and Skoyles , 1974
	<i>D. curranii</i>	Musgrave and Skoyles , 1974
	<i>D. evena</i>	Musgrave and Skoyles , 1974
	<i>D. kaki</i>	Matsura and Iinuma, 1977; Lin, <i>et al.</i> ,1988
	<i>D. melanilau</i>	Singh and Prakash, 1988
	<i>D. melanoxyton</i>	Mallavadhani, <i>et al.</i> , 1998
	<i>D. montana</i>	Musgrave and Skoyles , 1974
	<i>D. moonii</i>	Herath, <i>et al.</i> , 1978
	<i>D. oblongiflora</i>	Herath, <i>et al.</i> , 1978
	<i>D. peregrina</i>	Gupta and Tiwari, 1964b
	<i>D. tomentosa</i>	Bhakuni, <i>et al.</i> , 1971
	Olean-12-ene-3-one (106)	<i>D. morrisiana</i>

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Oleanolic acid acetate (107)	<i>D. eriantha</i> <i>D. lotus</i>	Chen, Yu and Huang, 1992 Zakaria, <i>et al.</i> , 1984
Oleanolic acid palmitate (108)	<i>D. montana</i>	Misra <i>et al.</i> , 1972
Oleanolic acid stearate (109)	<i>D. montana</i>	Misra <i>et al.</i> , 1972
Oleanolic acid glycoside (110-113)	<i>D. peregrina</i> <i>D. zombensis</i>	Gupta and Tiwari, 1964 Gafner <i>et al.</i> , 1987 ; Gafner and Rodriguez, 1988
Maslinic acid methyl ester (114)	<i>D. melanoxylon</i>	Mallavadhani, <i>et al.</i> , 2001
Morolic acid (115)	<i>D. melanonilau</i>	Mallavadhani, <i>et al.</i> , 1998

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Allobetulin (116)	<i>D. montana</i>	Yoshihira, <i>et al.</i> , 1971a
Oxyallobetulin (117)	<i>D. lotus</i> <i>D. montana</i> <i>D. morriisiana</i>	Bhakani, <i>et al.</i> , 1971 ; Yoshihira, <i>et al.</i> , 1971b Lillie, <i>et al.</i> , 1976a Yoshihira, <i>et al.</i> , 1971b
4. Taraxerane type		
Taraxerol (118)	<i>D. cordifolia</i> <i>D. ferrea</i> <i>D. hirsuta</i> <i>D. kaki</i> <i>D. lotus</i> <i>D. mollis</i> <i>D. morrisiana</i> <i>D. nicaraguensis</i>	Chandra and Shastri, 1989 Bhakuni <i>et al.</i> , 1971 Herath, <i>et al.</i> , 1978 Zhong and Feng, 1987 Bhakuni <i>et al.</i> , 1971 ; Yoshihira, <i>et al.</i> , 1971b Yoshihira, <i>et al.</i> , 1971a Yoshihira, <i>et al.</i> , 1971b Hasbun, <i>et al.</i> , 1988

Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Taraxerol (118)	<i>D. villosiuscula</i>	Khan and Timi, 1999c
Taraxerone (119)	<i>D. acuta</i> <i>D. ferrea</i> <i>D. lotus</i> <i>D. maritima</i> <i>D. rhodocalyx</i> <i>D. moonii</i> <i>D. oblongifolia</i> <i>D. oppositifolia</i> <i>D. quaesita</i> <i>D. rheophytica</i> <i>D. thwaitasii</i>	Herath, <i>et al.</i> , 1978 Bhakuni <i>et al.</i> , 1971 Zakaria, <i>et al.</i> , 1984 Kuo <i>et al.</i> , 1997c Sutthivaiyakit <i>et al.</i> , 1995 Herath, <i>et al.</i> , 1978 Herath, <i>et al.</i> , 1978 Herath, <i>et al.</i> , 1978 Herath, <i>et al.</i> , 1978 Herath, <i>et al.</i> , 1978 Herath, <i>et al.</i> , 1978

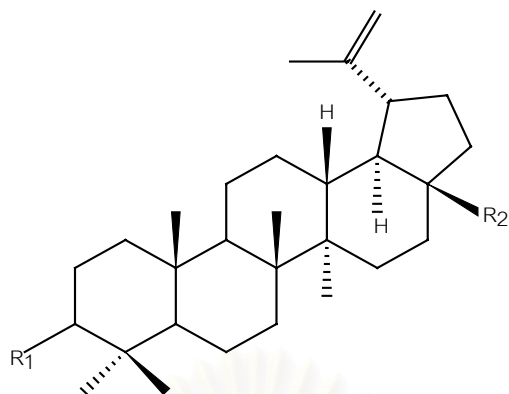
Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Taraxeryl acetate (120)	<i>D. maingayi</i>	Zakaria, <i>et al.</i> , 1984
5. Friedelane type and miscellaneous	<i>D. singaporensis</i>	Zakaria, <i>et al.</i> , 1984
Friedelin (121)	<i>D. eriantha</i>	Chen <i>et al.</i> , 1992
	<i>D. ferrea</i>	Tiwari, Masood and Minocha, 1979
	<i>D. maritima</i>	Higa, Orihara and Yogi, 1998
	<i>D. undulata</i> var. <i>cratericalyx</i>	Aoonpakh, 2001
Friedelin-3-ol (122)	<i>D. eriantha</i>	Chen <i>et al.</i> , 1994
	<i>D. ferrea</i>	Tiwari, <i>et al.</i> , 1979
2 α -Hydroxyfriedelin (123)	<i>D. iturensis</i>	Zhong, <i>et al.</i> , 1984
	<i>D. sanza-minika</i>	Zhong, <i>et al.</i> , 1984

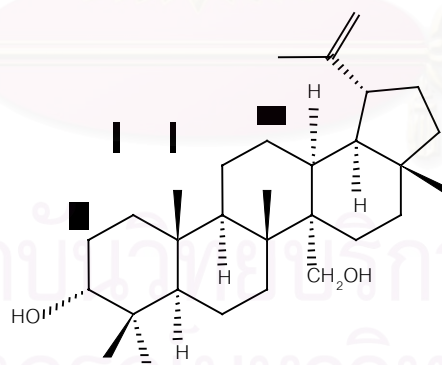
Table 2. Distribution of triterpenoids in the genus *Diospyros* (continued)

Compounds	Sources	References
Glut-5(6)-ene-3- β -ol (124)	<i>D. iturensis</i> <i>D. sanza-minika</i>	Zhong, <i>et al.</i> ,1984 Zhong, <i>et al.</i> ,1984

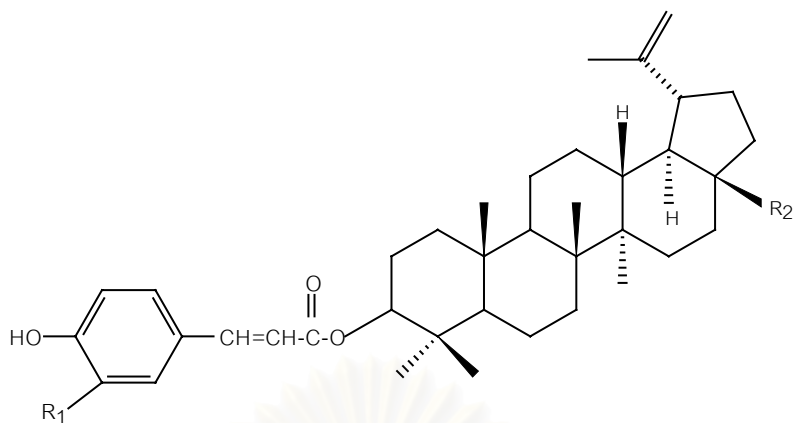
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Lupeol (72)	$R_1 = \beta\text{-OH}$	$R_2 = \text{CH}_3$
Epi-lupeol (73)	$R_1 = \alpha\text{-OH}$	$R_2 = \text{CH}_3$
Lupenone (74)	$R_1 = =\text{O}$	$R_2 = \text{CH}_3$
Betulin (75)	$R_1 = \beta\text{-OH}$	$R_2 = \text{CH}_2\text{OH}$
Betulinic acid (76)	$R_1 = \beta\text{-OH}$	$R_2 = \text{COOH}$
Betunaldehyde (77)	$R_1 = \beta\text{-OH}$	$R_2 = \text{CHO}$



Peregrinol (78)



3-(*Z*)-Coumaroyllupeol (79) $R_1 = H$

$R_2 = CH_3$

3-(*E*)-Coumaroyl-28-palmitoylbetulin (80) $R_1 = H$

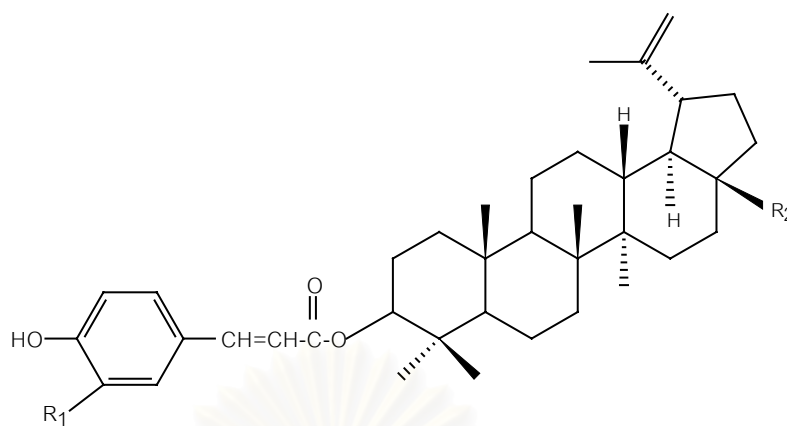
$R_2 = CH_2-O-C(=O)-(CH_2)_{14}CH_3$

3-(*Z*)-Coumaroyl-28-palmitoylbetulin (81) $R_1 = H$

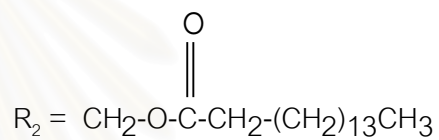
$R_2 = CH_2-O-C(=O)-(CH_2)_{14}CH_3$

3-(*E*)-Feruloylbetulin (82) $R_1 = -OCH_3$

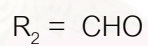
$R_2 = CH_2OH$



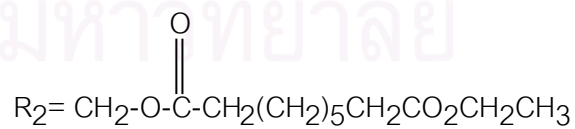
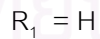
3-(*E*)-Feruloyl-28-palmitoylbetulin (**83**) $R_1 = -OCH_3$



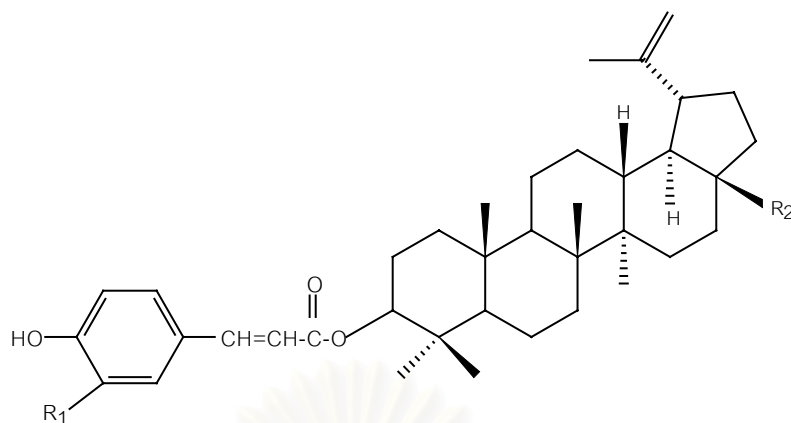
3-(*E*)-Coumaroylbetulin aldehyde (**84**) $R_1 = H$



3-(*E*)-Coumaroylbetulin-28-yl ethyl nonanedioate (**85**)

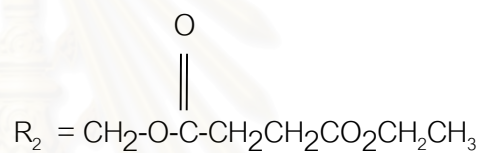


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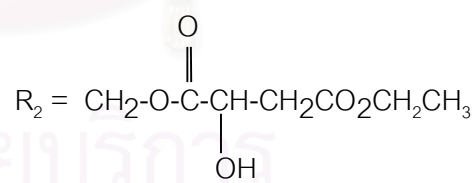
3-(*E*)-Coumaroylbetulin-28-yl ethylsuccinate (**86**)

$$R_1 = H$$



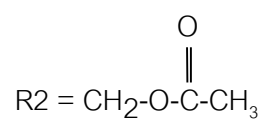
3-(*E*)-Coumaroylbetulin-28-yl ethyl (2*R*)-2-hydroxysuccinate (**87**)

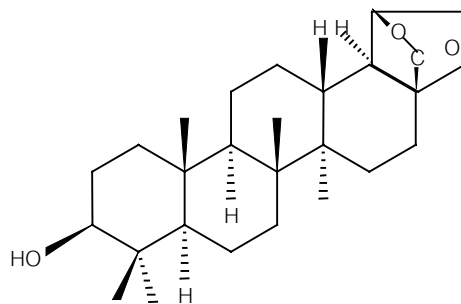
$$R_1 = H$$



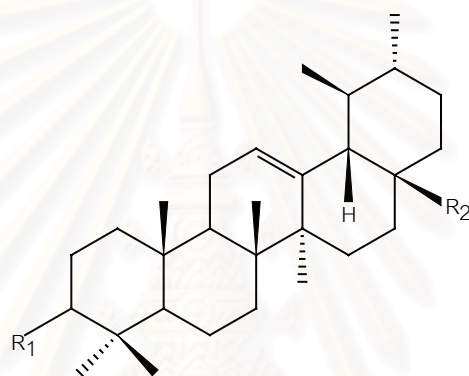
28-Acetyl-3-(*E*)-coumaroylbetulin (**88**)

$$R_1 = H$$

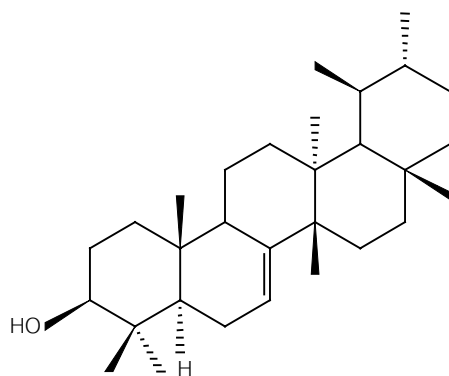




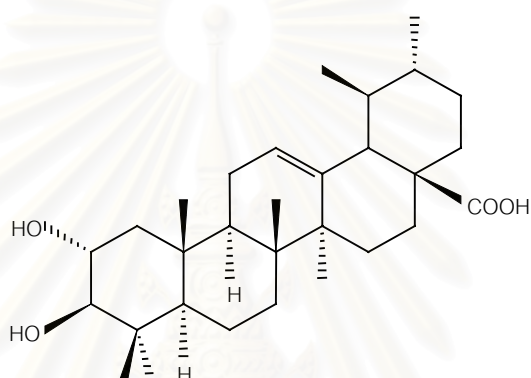
Diospyrolide (89)



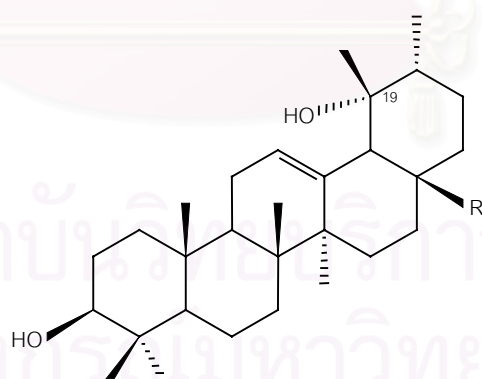
α -Amyrin (90)	$R_1 = \beta\text{-OH}$	$R_2 = \text{CH}_3$
α -Amyrone (91)	$R_1 = =\text{O}$	$R_2 = \text{CH}_3$
Ursolic acid (92)	$R_1 = \beta\text{-OH}$	$R_2 = \text{COOH}$
Ursolic acid acetate (93)	$R_1 = \beta\text{-OCOCH}_3$	$R_2 = \text{COOH}$
Ursolic acid palmitate (94)	$R_1 = \beta\text{-OCO(CH}_2\text{)}_{14}\text{CH}_3$	$R_2 = \text{COOH}$
Ursolic acid stearate (95)	$R_1 = \beta\text{-OCO(CH}_2\text{)}_{16}\text{CH}_3$	$R_2 = \text{COOH}$
Uvaol (96)	$R_1 = \beta\text{-OH}$	$R_2 = \text{CH}_2\text{OH}$
Epi-uvaol (97)	$R_1 = \alpha\text{-OH}$	$R_2 = \text{CH}_2\text{OH}$



Bauerenol (98)

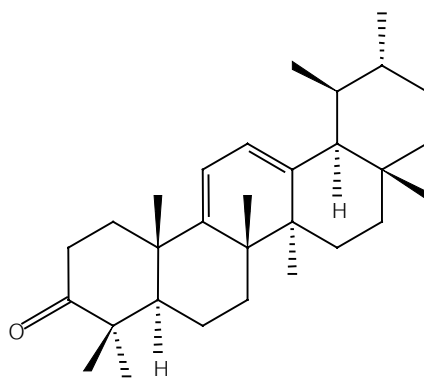


Corsalic acid (99)

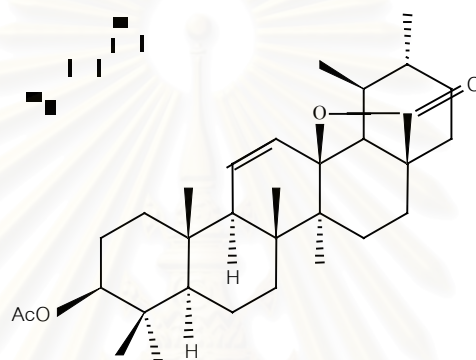


19 α -Hydroxyursolic acid (100) R= COOH

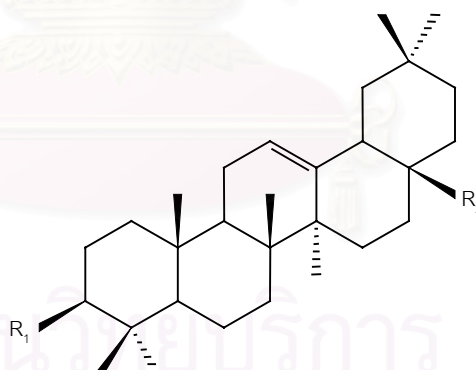
Pomolic acid methylester(101) R= COOCH₃



Marsfomosanone (102)



3β-Acetoxy-urs-11-ene-28,13-olide (103)



β-Amyrin (104)

 $R_1 = \beta\text{-OH}$ $R_2 = \text{CH}_3$

Oleanolic acid(105)

 $R_1 = \beta\text{-OH}$ $R_2 = \text{COOH}$

Olean-12-ene-3-one(106)

 $R_1 = =\text{O}$ $R_2 = \text{CH}_3$

Oleanolic acid acetate (107)

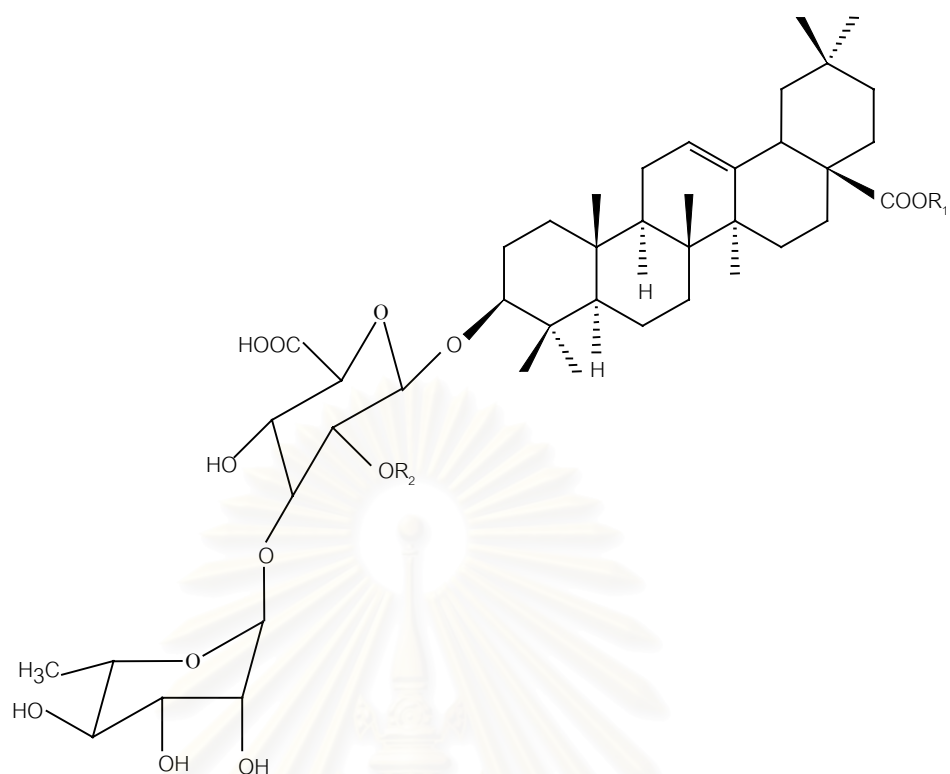
 $R_1 = \text{OCOCH}_3$ $R_2 = \text{COOH}$

Oleanolic acid palmitate (108)

 $R_1 = \text{OCO}(\text{CH}_2)_{14}\text{CH}_3$ $R_2 = \text{COOH}$

Oleanolic acid stearate (109)

 $R_1 = \text{OCO}(\text{CH}_2)_{16}\text{CH}_3$ $R_2 = \text{COOH}$

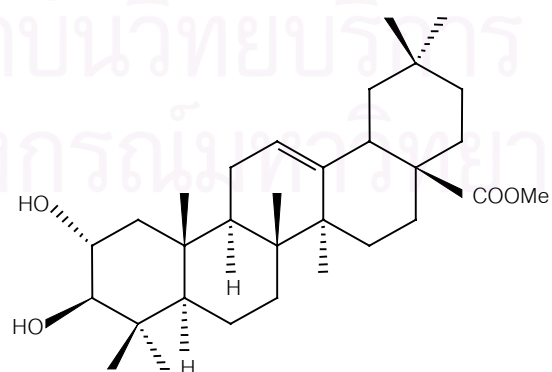


Oleanolic acid glycoside ; (110) R1 = R2 = H

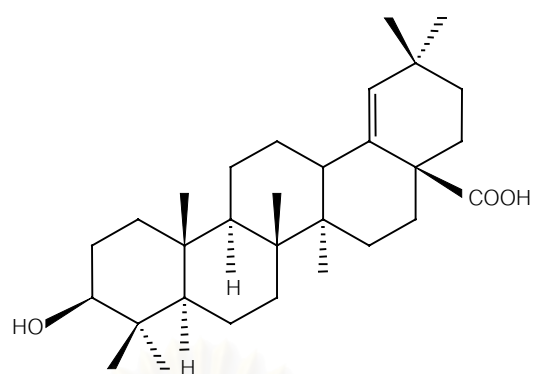
(111) R1 = Glucosyl R2 = H

(112) R1 = Glucosyl R2 = Xylosyl

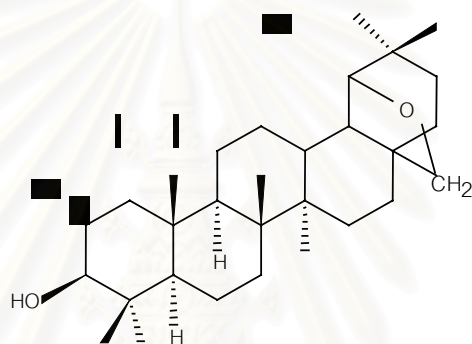
(113) R1 = H R2 = Xylosyl



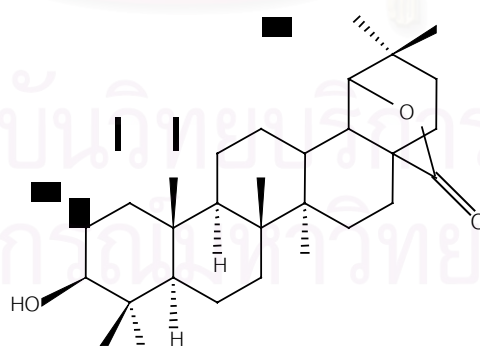
Maslinic acid methyl ester (114)



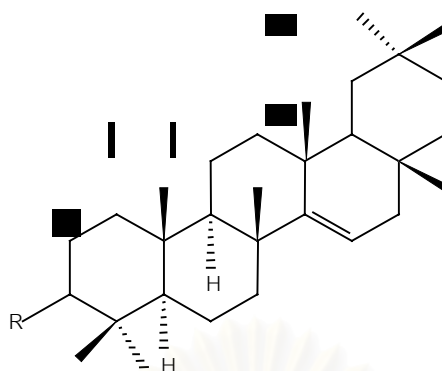
Morolic acid (115)



Alobetulin (116)



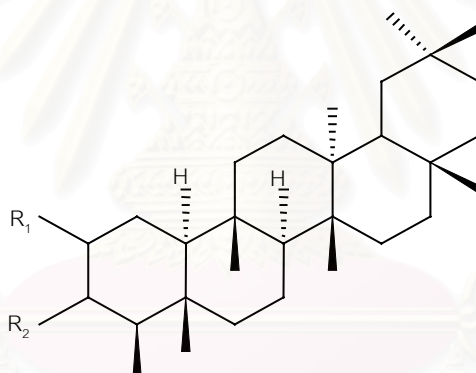
Oxyallobetulin (117)



Taraxerol (118) $R = \beta\text{-OH}$

Taraxerone (119) $R = =\text{O}$

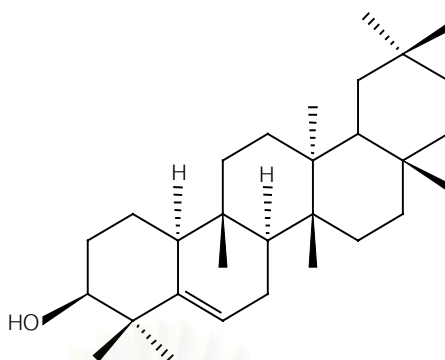
Taraxeryl acetate (120) $R = \beta\text{-OCOCH}_3$



Friedelin (121) $R_1 = \text{H}$ $R_2 = =\text{O}$

Friedelin-3-ol (122) $R_1 = \text{H}$ $R_2 = \alpha\text{-OH}$

2 α -Hydroxyfriedelin (123) $R_1 = \alpha\text{-OH}$ $R_2 = =\text{O}$



Glut-5(6)-ene-3 β -ol (124)



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CHAPTER III

EXPERIMENTAL

Source of Plant Material

The stems of *Diospyros glandulosa* Lace were collected from Doi Phuka National Park, Nan province, Thailand, in May 2000. The plant material was identified by comparison with the herbarium specimens (KBF no. 130012) at the Royal Forest Department, Ministry of Agriculture and Co-operative, Bangkok, Thailand.

General Techniques

1. Chromatographic Technique

1.1 Thin- Layer Chromatography (TLC)

Technique	: One dimension, ascending
Adsorbent	: Silica gel 60 F254 (E. Merck) precoated plate, layer thickness 0.2 mm
Solvent system	: Various solvent systems depending on materials
Distance	: 7 cm
Temperature	: 25-35°C (room temperature)
Detection	: 1) UV light (254 and 365 nm) 2) 10% sulfuric acid in ethanol, heating at 110°C for 5-10 minutes 3) anisaldehyde – sulfuric acid reagent, heating at 110°C for 5-10 minutes 4) Liebermann-Burchard reagent

1.2 Column Chromatography (CC)

Column	: Flat bottom glass column (various diameters)
Adsorbent	: Silica gel 60 (No. 9385, E. Merck) particle size 0.040-0.063 nm (230-400 mesh ASTM)
Packing method	: Wet packing
Sample loading	: 1) Dry packing

The sample was dissolved in a small volume of organic solvent, mixed with a small quantity of adsorbent, triturated, dried and then loaded on the top of the column.

2) Wet packing

The sample was dissolved in a small volume of the eluent, then loaded on the top of the column.

Solvent system	: Various solvent systems depending on materials
Detection	: Fractions were examined by TLC observed under UV light at the wavelengths of 254 and 365 nm. The TLC plate was then sprayed with 10% sulfuric acid in ethanol and heated at 110°C for 5-10 minutes. Fractions of similar chromatographic pattern were combined.

2. Spectroscopy

2.1 Infrared (IR) Absorption Spectra

IR spectra (KBr disc) were obtained on a Perkin Elmer infrared spectrophotometer Model 283 (Pharmaceutical Research Equipment Center, Faculty of Pharmaceutical Sciences, Chulalongkorn University).

2.2 Mass Spectra (MS)

Electron Impact Mass Spectra (EIMS) were obtained on a Polaris Q Finnigan Gas Chromatography – Mass Spectrometer (Department of Chemistry, Faculty of Science, Mahidol University), operating at 50 eV.

2.3 Proton and Carbon 13 Nuclear Magnetic Resonance (^1H - and ^{13}C -NMR) Spectra

The ^1H -NMR (300 MHz) and ^{13}C -NMR (75 MHz) spectra were obtained with a Bruker Avance DPX-300 FT-NMR spectrometer (Faculty of Pharmaceutical Sciences, Chulalongkorn University).

The ^1H -NMR (500 MHz) spectra were obtained with a JEOL JNM-A500 (Alpha series) 500 MHz NMR spectrometer (Scientific and Technological Research Equipment Center, Chulalongkorn University).

NMR solvents used in this study were deuterated dimethylsulfoxide (DMSO-d_6) and deuterated chloroform (CDCl_3). Chemical shifts were reported in ppm scale using the chemical shift of the solvent as the reference signal.

3. Melting Points

Melting points were obtained on a Fisher/Johns melting point apparatus (Department of Pharmaceutical Botany, Faculty of Pharmaceutical Sciences, Chulalongkorn University). The melting points were uncorrected.

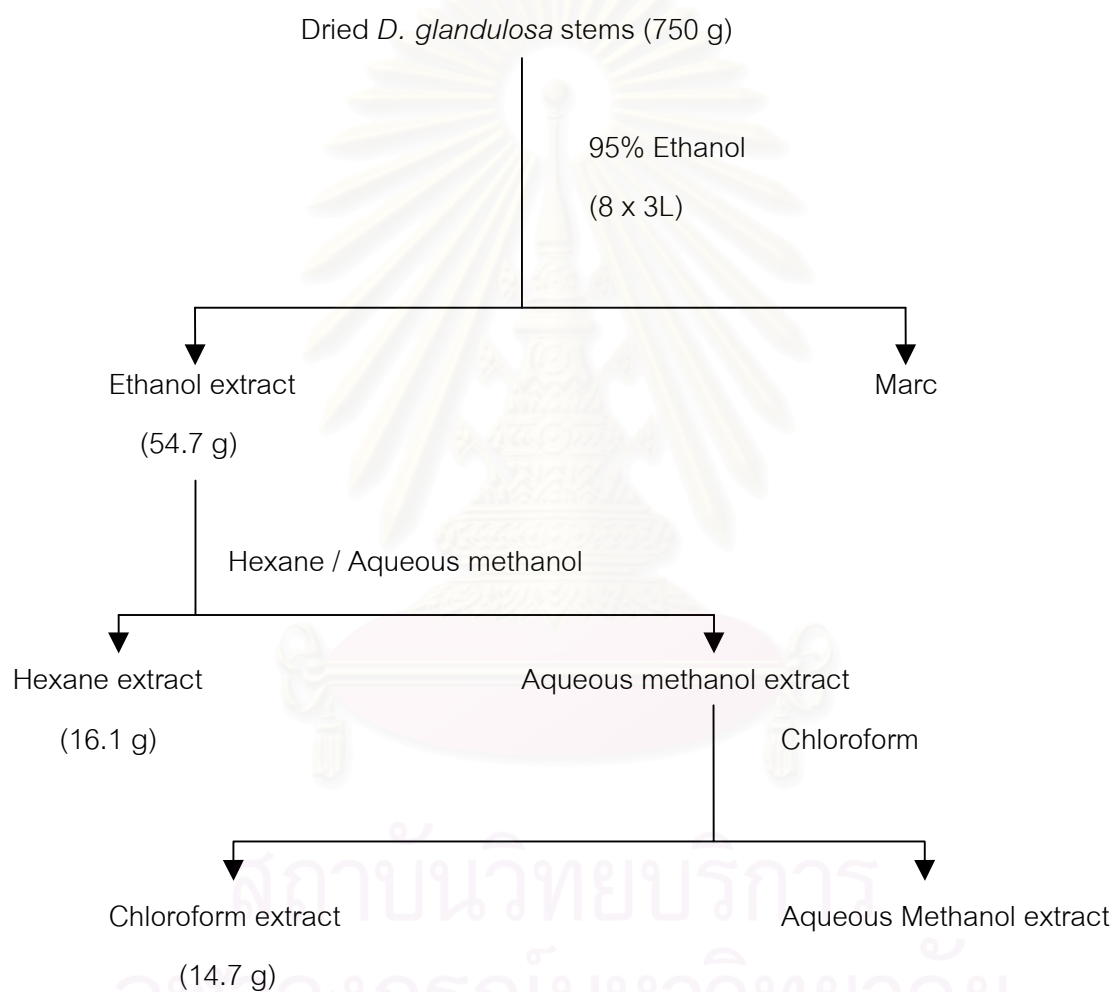
4. Solvent

All organic solvents used in the extraction and isolation procedure were of commercial grade and were redistilled prior to used.

Extraction Procedure

The dried stems of *Diospyros glandulosa* Lace (750 g) were ground into small pieces, macerated eight times in 95% ethanol (3L x 3 days each) and then filtered. The filtrate of each batch was combined and concentrated by removing ethanol under reduced pressure to yield 54.7 g of dried crude extract (7.29% of dry weight). The ethanol extract was diluted with aqueous methanol and partitioned with hexane (12x1.5L) to give hexane

extract (16.1 g, 2.15% of dry weight). The aqueous methanol layer was then partitioned with chloroform (12x1.5L) to give 14.7g (1.96% of dried weight) of chloroform extract.



Scheme 1. Extraction of *Diospyros glandulosa* stems

Isolation Procedure

1. Fractionation of the Hexane Extract

The hexane extract (10.6 g) was subjected to a silica gel column (250 g, 5 x 60 cm) and eluted with solvent mixtures of increasing polarity (hexane-chloroform to chloroform-methanol). Three hundred 30-ml fractions were collected and combined according to their TLC patterns into seven major fractions (F001-F007) as shown in Table 3. The column was then washed down with methanol.

Table 3. Combined fractions from the hexane extract

Fraction	Solvent ratio (hexane : CHCl ₃ : MeOH)	Number of eluates	Weight (g)
F001	60:40:0	1-32	0.67
F002	40:60:0	33-96	1.96
F003	30:70:0	97-139	1.61
F004	20:80:0	140-197	1.74
F005	0:100:0	198-241	1.43
F006	0:98:2	242-263	0.58
F007	0:95:5	264-300	0.92
Methanol eluate			0.99

1.1 Isolation of Compound DG1

Fraction F002, which gave a major yellow spot upon TLC investigation with anisaldehyde-sulfuric acid reagent, was further purified by recrystallization in methanol to give compound DG1 as colorless needles (50.3 mg).

1.2 Isolation of Compound DG2

Fraction F004 (1.74 g) was subjected to a silica gel column (100 g, 5x50 cm), using chloroform - methanol (99:1) as the eluent. Ninety fractions (5 ml each) were collected and combined according to their TLC patterns into five major fractions (F008 - F011) as shown in Table 4.

Table 4. Combined fractions from F004

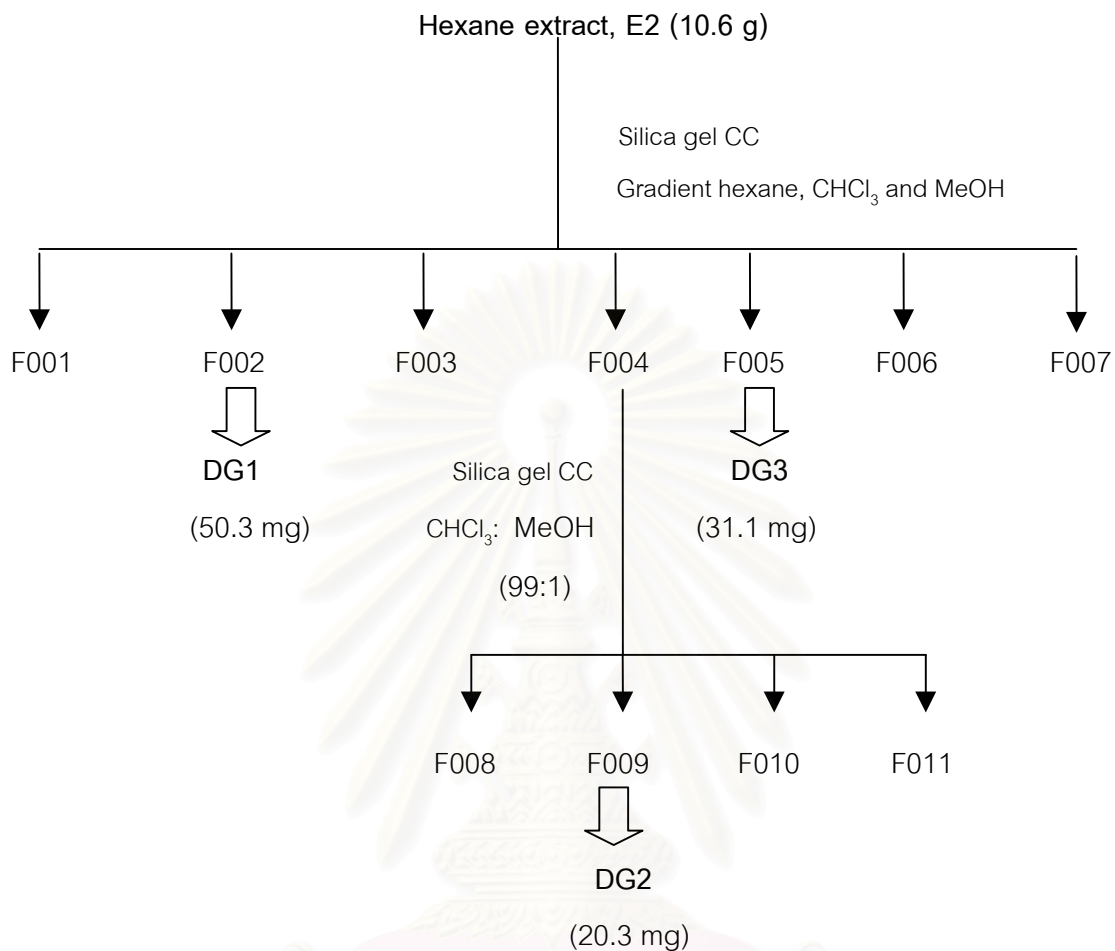
Fraction	Number of eluates	Weight (mg)
F008	1-24	216.2
F009	25-52	514.9
F010	53-71	243.1
F011	72-90	227.8

Fraction F009, which appeared as a pink-violet spot upon TLC investigation with 10% ethanolic sulfuric acid reagent, was purified by recrystallization in methanol to give compound DG2 as colorless needles (20.3 mg).

1.3 Isolation of Compound DG3

Fraction F005 gave a major red-violet spot upon TLC investigation with 10% ethanolic sulfuric acid reagent. This fraction was further purified by recrystallization in methanol to give compound DG3 as white powder (33.1 mg).

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Scheme 2. Isolation of the hexane extract

2. Fractionation of the Chloroform Extract

The chloroform extract (14.7 g) was divided into 2 parts: A (8.6g) and B (5.3g). Fraction A (8.6 g) was subjected to a silica gel column (300 g, 5 x 60 cm) using chloroform-methanol mixtures of increasing polarity as the eluent. Two hundred and fifty 30-ml fractions were collected and combined according to their TLC patterns into seven major fractions (F012 - F018) as shown in Table 5. The column was then washed down with methanol.

Table 5. Combined fractions from the chloroform extract

Fraction	Solvent ratio (CHCl ₃ : MeOH)	Number of eluates	Weight (g)
F012	100:0	1-10	0.65
F013	99:1	11-32	0.64
F014	98:2 to 95 : 5	33-128	2.02
F015	93:7	129-154	0.69
F016	90:10	155-176	0.81
F017	85:15	177-213	0.96
F018	80 : 20	214-250	0.88
Methanol eluate			1.01

2.1 Isolation of Compound DG4

Fraction F013 (0.64 g), which gave interesting spots upon TLC investigation, was submitted to further separation on a silica gel column (30 g, 2.5x50 cm) eluted with chloroform. Sixty 5-ml fractions were combined into five major fractions (F019 - F023) as shown in Table 6.

Table 6. Combined fractions from F013

Fraction	Number of eluates	Weight (mg)
F019	1-17	96.7
F020	18-39	122.4
F021	40-62	137.6
F022	63-78	109.3
F023	79-90	100.4

Fraction F021, which gave a red-violet spot on TLC upon detection with 10% ethanolic sulfuric acid reagent, was further purified by recrystallization in methanol. White amorphous powder (41.1 mg) was obtained and designated as compound DG4.

2.2 Isolation of Compound DG5

Fraction F014, which gave interesting TLC profile, was selected for further investigation. The sample (2.02 g) was chromatographed on a silica gel column (100 g, 5x50 cm) using chloroform - methanol (99:1) as the eluent. One hundred and twenty fractions (10 ml each) were collected and combined according to their TLC patterns into five major fractions (F024 - F028) as shown in Table 7.

Table 7. Combined fractions from F014

Fraction	Number of eluates	Weight (mg)
F024	1-35	344.2
F025	36-52	201.4
F026	53-66	186.6
F027	67-88	248.8
F028	89-120	743.2

Fraction F028 was further separated on a silica gel column (30 g, 2x50 cm) eluted with chloroform - methanol (99:1). One hundred fractions (5 ml each) were collected and, later, pooled into four major fractions (F029 - F032) as shown in Table 8.

Table 8. Combined fractions from F028

Fraction	Number of eluates	Weight (mg)
F029	1-26	114.1
F030	27-64	321.2
F031	65-87	132.8
F032	88-100	102.1

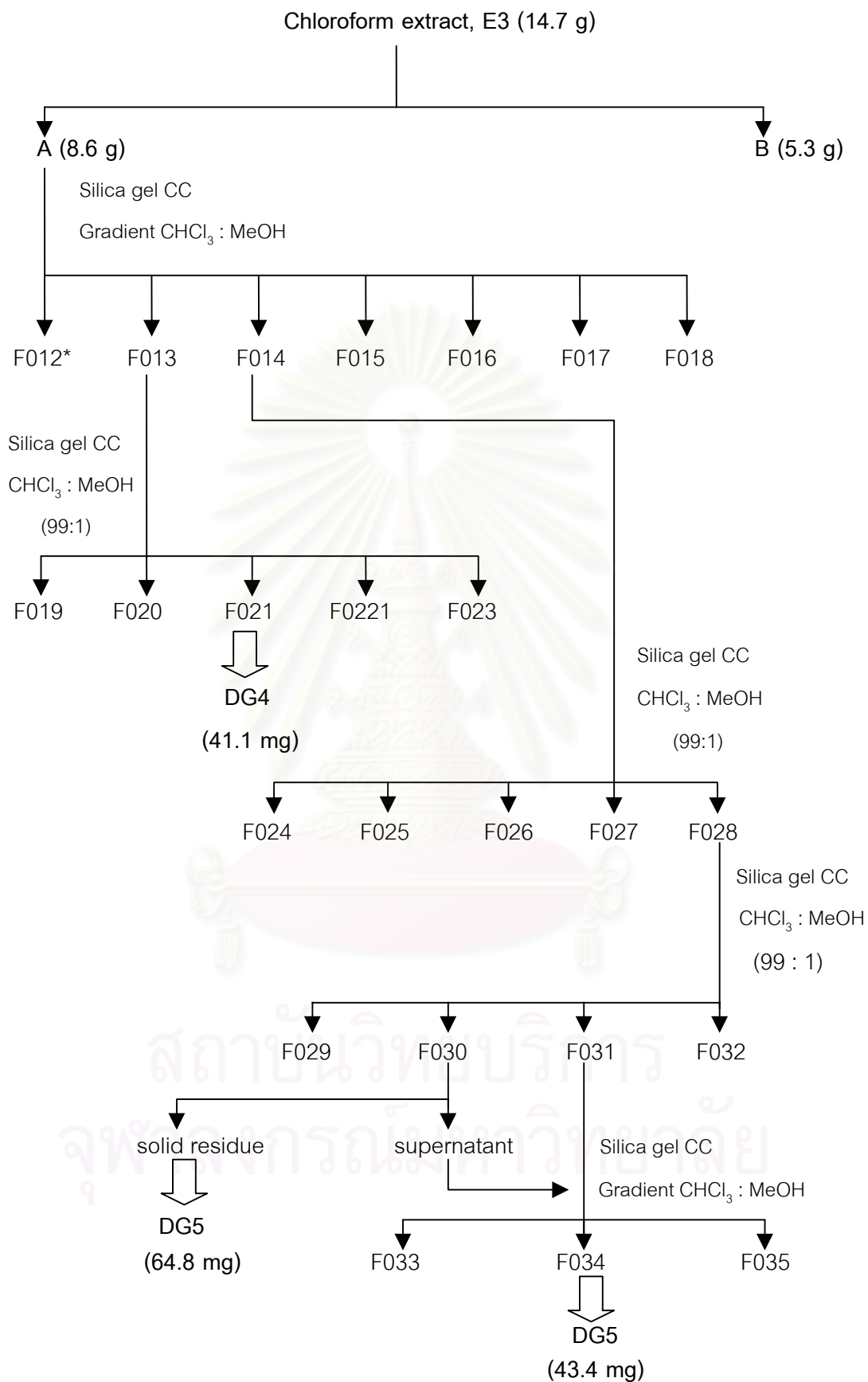
Fraction F030 gave a major pink-violet spot on TLC when detected with 10% ethanolic sulfuric acid reagent. When dissolved in hexane, it could be separated into 2 parts: solid residue and supernatant. The solid residue was filtered and recrystallized in hexane to give compound DG5 as colorless prisms (64.8 mg).

The supernatant was combined with F031 for further isolation. The sample (241.4 mg) was rechromatographed on a silica gel column (15 g, 2x50 cm), eluted stepwise with chloroform-methanol. One hundred 5-ml fractions were collected and combined according to their TLC patterns into three major fractions (F033-F035) as shown in Table 9.

Table 9. Combined fractions from F031

Fraction	Solvent ratio (CHCl ₃ : MeOH)	Number of eluates	Weight (mg)
F033	98 : 2	1-18	66.3
F034	97 : 3	19-74	121.4
F035	95 : 5	75-100	71.8

Compound DG5 was obtained as colorless prisms (43.4 mg) upon recrystallization of F034 in hexane.



Scheme 3. Isolation of the chloroform extract (A)

2.3 Isolation of Compound DG6

The other portion of chloroform extract, named fraction B (5.3 g), was subjected to silica gel column chromatography (250 g, 5 x 50 cm) by elution with chloroform – methanol of increasing polarity. One hundred and fifty 30-ml fractions were collected and combined according to their TLC patterns into five major fractions (F036-F040), as shown in Table 10. The column was then washed down with methanol.

Table 10. Combined fractions from the chloroform extract (B)

Fraction	Solvent ratio (CHCl ₃ : MeOH)	Number of eluates	Weight (mg)
F036	100 : 0	1-14	0.60
F037	99 : 1	15-33	0.63
F038	97 : 3	34-76	1.14
F039	95 : 5	77-112	0.83
F040	90 : 10	113-150	0.91
Methanol eluate			0.98

Fraction F038, which gave an interesting spot upon TLC investigation, was submitted for further isolation on a silica gel column (60 g, 2.5x50 cm), eluted with a gradient of chloroform-acetone. One hundred and fifty 15-ml fractions were collected and combined according to their TLC patterns into five major fractions, (F041 -F045), as shown in Table 11.

Table 11. Combined fractions from F038

Fraction	Solvent ratio (CHCl ₃ : acetone)	Number of eluates	Weight (mg)
F041	97 : 3	1-14	0.60
F042	97 : 3	15-33	0.63
F043	95 : 5	34-76	1.14
F044	95 : 5	77-112	0.83
F045	90 : 10	113-150	0.91

Fraction F043 gave major pink-violet spot on TLC upon detection with 10% ethanolic sulfuric acid reagent. Dissolved in methanol, it could be separated into 2 parts: solid residue and supernatant. The solid residue was filtered and recrystallized in methanol to give compound DG6 as colorless needles (29.6 mg).

The supernatant and F044, both which gave the same TLC pattern, were combined together for further separation. The sample (333.6 mg) was rechromatographed on a silica gel column (20 g, 2x50 cm) using chloroform - acetone (95:5) as the eluent. One hundred and twenty 5-ml fractions were collected and combined according to their TLC patterns into four major fractions (F046 - F049) as shown in Table 12.

Table 12. Combined fractions from F043 and F044

Fraction	Number of eluates	Weight (mg)
F046	1-47	114.2
F047	48-59	20.8
F048	60-96	91.4
F049	97-120	48.7

Compound DG6 was obtained as colorless needles (20.8 mg) upon recrystallization of fraction F047 in methanol.

2.4 Isolation of Compound DG3

Fraction F012 (0.65 g) and fraction F036 (0.60 g) showed a red-violet spot on TLC upon detection. These two fractions were combined together and then further separated on a silica gel column (60 g, 2.5x50 cm) eluted with chloroform. Sixty fractions (15 ml each) were collected and combined according to their TLC patterns into three major fractions (F050 - F052), as shown in Table 13.

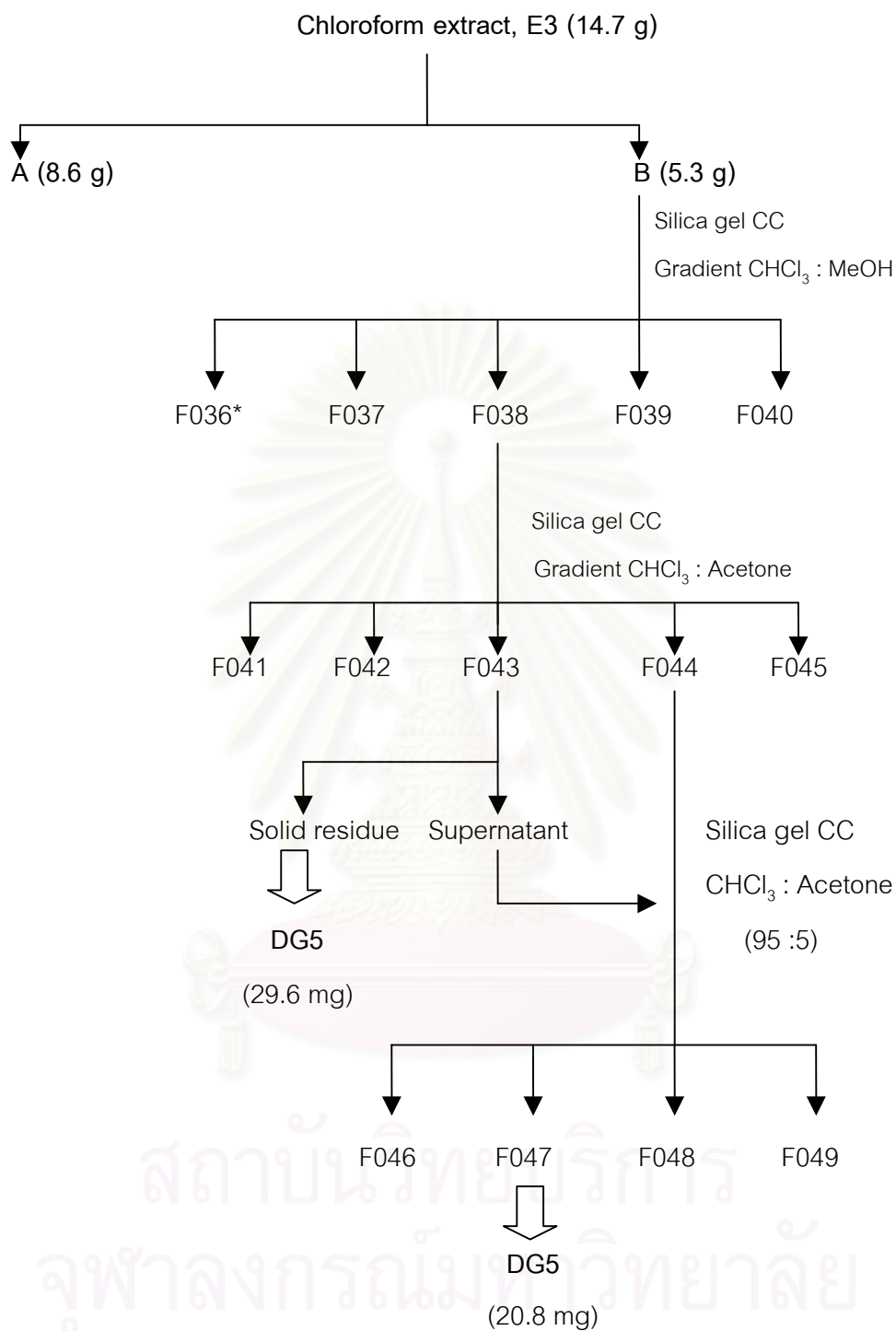
Table 13. Combined fractions from F012 and F036

Fraction	Number of eluates	Weight (mg)
F050	1-19	214.8
F051	20-37	416.3
F052	38-60	431.7

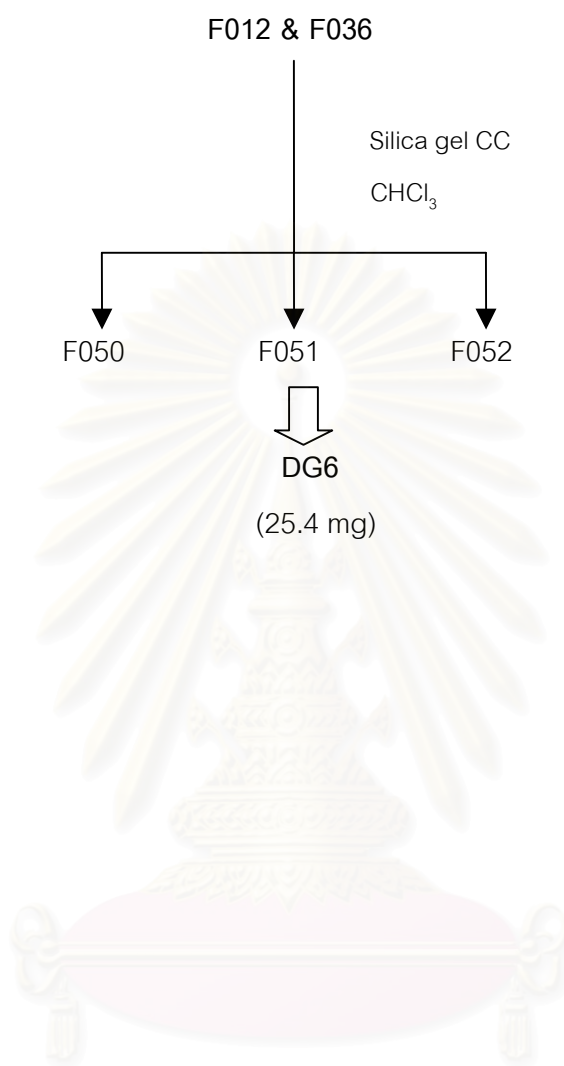
Fraction F051 was further purified by recrystallization in methanol to give a pure compound as white powder (25.4 mg). The compound was suggested by TLC comparison to be identical with compound DG3 which previously obtained from the hexane extract.



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Scheme 4. Isolation of the chloroform extract (B)



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Scheme 5. Isolation of fraction F022 and fraction F040

All isolated compounds were tested with Liebermann-Burchard reagent and the result are shown in Table 14. The total amount of each compound obtained from the plant material is also shown in the same table.

Table 14. Results of Liebermann-Burchard test and the total amount of the isolated compounds

Compounds	Color with Liebermann-Burchard test	Total amount	
		Weight (mg)	% yield
DG1	Purple	50.3	0.01
DG2	Purple	20.3	0.004
DG3	Red-violet	58.5	0.01
DG4	Red-violet	41.1	0.01
DG5	Purple	108.2	0.02
DG6	Purple	50.4	0.01

Characterization of isolated compounds

1. Compound DG1

Appearance : Colorless needles (methanol)

Solubility : Soluble in hexane and chloroform

Melting point : 262-263 °C

EIMS m/z (% relative intensity) : 426(27), 341(24), 302(22), 273(62), 246(66), 231(84),
123(80), 109(100), 95(98) and 81(79)

(Figure 2, page 116)

IR ν_{\max} (KBr disc) cm^{-1} : 3404, 2927, 1714, 1463, 1388, 1049 and 788

(Figure 3, page 117)

^1H - NMR (δ ppm, 300 MHz, CDCl_3): 0.70 (3H, s), 0.85 (3H, s), 0.86 (3H, d, $J = 6.0$ Hz),
0.93 (3H, s), 0.98(6H, s), 1.03(3H, s), 1.16(3H, s),
2.23 (1H, m), 1.37 (1H, m)

(Figure 4, page 118)

^{13}C - NMR (δ ppm, 75 MHz, CDCl_3): 6.8, 14.6, 17.9, 18.2, 18.6, 20.2, 22.3, 28.2, 30.0,
30.5, 31.8, 32.1, 32.4, 32.8, 35.0, 35.3, 35.6, 36.0,
37.4, 38.3, 39.2, 39.7, 41.3, 41.5, 42.1, 42.8, 53.1,
58.2, 59.5 and 213.2

(Figure 6, page 122)

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2. Compound DG2

Appearance : Colorless needles (methanol)

Solubility : Soluble in chloroform, acetone

Melting point : 195-196 °C

EIMS m/z (% relative intensity) : 426(10), 218(100), 203(35) and 189(12)

(Figure 9, page 132)

IR ν_{\max} (KBr disc) cm^{-1} : 3282, 2947, 1464, 1386, 1360, 996 and 660

(Figure 10, page 133)

^1H -NMR (δ ppm, 300 MHz, CDCl_3): 0.77(3H, s), 0.81(3H, s), 0.85(6H, s), 0.92(3H, s), 0.95(3H, s), 0.98(3H, s), 1.12(3H, s), 3.20 (1H, *dd*, $J=10.7, 5.0$ Hz) and 5.17(1H, *br t*)

(Figure 11, page 134)

^{13}C -NMR (δ ppm, 75 MHz, CDCl_3): 15.5, 15.6, 16.8, 18.4, 23.6, 23.7, 26.0, 26.1, 26.9, 27.2, 28.1, 28.4, 31.1, 32.5, 32.6, 33.3, 34.7, 36.9, 37.1, 38.6, 38.8, 39.8, 41.7, 46.8, 47.2, 47.6, 55.2, 79.0, 121.7 and 145.2

(Figure 13, page 138)

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3. Compound DG3

Appearance : White powder (methanol)

Solubility : Soluble in chloroform

Melting point : 214-215 °C

EIMS m/z (% relative intensity) : 426(25), 411(25), 393(10), 218(93), 204(82), and 189(100)

(Figure 16, page 149)

IR ν_{\max} (KBr disc) cm^{-1} : 3486, 2934, 1474, 1443, 1384, 1037 and 815

(Figure 17, page 150)

^1H -NMR (δ ppm, 300 MHz, CDCl_3): 0.66(1H, *d*, $J=8.7$ Hz), 0.74(3H, *s*), 0.76(3H, *s*), 0.81(3H, *s*), 0.92(3H, *s*), 0.94(3H, *s*), 1.01(3H, *s*), 1.66 (3H, *s*), 2.36 (1H, *m*), 3.17 (1H, *m*), 4.55 (1H, *br s*) and 4.67(1H, *br s*)

(Figure 18, page 151)

^{13}C -NMR (δ ppm, 75 MHz, CDCl_3): 14.5, 15.4, 16.0, 16.1, 18.0, 18.3, 19.3, 20.9, 25.1, 27.4, 28.0, 30.0, 34.3, 35.6, 37.2, 38.0, 38.7, 38.9, 40.0, 40.8, 42.8, 43.0, 48.0, 48.3, 50.4, 55.3, 79.0, 109.3 and 151.0

(Figure 19, page 153)

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4. Compound DG4

Appearance	: White amorphous powder (methanol)
Solubility	: Soluble in chloroform, acetone
Melting point	: 251-252 °C
EIMS m/z (% relative intensity)	: 442 (12), 234 (27), 207 (48), 203 (100), 189 (99), 175 (41), 47 (42), 133 (45), 119 (46), 95 (48) and 81(31)

(Figure 22, page 162)

IR ν_{\max} (KBr disc) cm^{-1}	: 3443, 2934, 2867, 1641, 1459, 1373, 1011 and 879
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(Figure 23, page 163)

^1H - NMR (δ ppm, 300 MHz, CDCl_3):	0.66(1H, <i>d</i> , $J= 9.3$ Hz), 0.74(3H, <i>s</i>), 0.80(3H, <i>s</i>), 0.95 (3H, <i>s</i>), 0.96(3H, <i>s</i>), 1.00(3H, <i>s</i>), 1.66(3H, <i>s</i>), 2.36 (1H, <i>m</i>), 3.16 (1H, <i>dd</i> , $J= 5.1, 10.8$ Hz), 3.31 (1H, <i>d</i> , $J= 10.8$ Hz), 3.78(1H, <i>d</i> , $J= 10.8$ Hz), 4.56 (1H, <i>s</i>) and 4.66(1H, <i>s</i>)
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(Figure 24, page 164)

^{13}C - NMR (δ ppm, 75 MHz, CDCl_3):	14.7, 15.3, 16.0, 16.1, 18.3, 19.1, 20.8, 25.2, 27.0, 27.3, 28.0, 29.2, 29.7, 33.9, 34.2, 37.1, 37.3, 38.7, 38.8, 40.9, 42.7, 47.8, 47.8, 48.7, 50.4, 55.3, 60.5, 79.0, 109.7 and 150.5
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(Figure 25, page 166)

5. Compound DG5

Appearance : Colorless prisms (hexane)

Solubility : Soluble in methanol

Melting point : 282-283 °C

EIMS m/z (% relative intensity) : 248(100), 219(26), 203(68) 189(22) and
133(61)

(Figure 28, page 176)

IR ν_{\max} (KBr disc) cm^{-1} : 3417, 2927, 1694, 1456, 1386, 1030, 997 and
759

(Figure 29, page 177)

^1H - NMR (δ ppm, 500 MHz, $\text{DMSO-}d_6$) : 0.67(3H, s), 0.74(3H, s), 0.80(3H, *d*, $J=6.4$
Hz), 0.86(3H, s), 0.88(3H, s), 0.89(3H, *d*,
 $J=8.85$ Hz), 1.03(3H, s), 2.10 (1H, *d*, $J=11.6$
Hz), 2.99 (1H, *dd*, $J= 5.2, 10.1$ Hz) and
5.12 (1H, *t*, $J= 3.4$ Hz)

(Figure 30, page 178)

^{13}C - NMR (δ ppm, 75 MHz, $\text{DMSO-}d_6$) : 15.2, 16.1, 16.9, 17.0, 18.0, 21.0, 22.8, 23.3,
23.8, 27.0, 27.5, 28.2, 30.2, 32.7, 36.3, 36.5,
38.2, 38.4, 38.5, 38.5, 39.1, 41.6, 46.8, 47.0,
52.4, 54.8, 76.8, 124.6, 138.2 and 178.3

(Figure 31, page 179)

6. Compound DG6

Appearance : Colorless needles (methanol)

Solubility : Soluble in chloroform

Melting point : 297 – 298 °C

EIMS m/z (% relative intensity) : 248(100), 207(26), 203(75) and 189(12)

(Figure 35, page 194)

IR ν_{\max} (KBr disc) cm^{-1} : 3432, 2948, 1695, 1463, 1386, 1182 and 1029

(Figure 36, page 195)

^1H - NMR (δ ppm, 300 MHz, CDCl_3): 0.70 (1H, s), 0.73 (3H, s), 0.75 (3H, s), 0.88 (3H, s),
0.89 (3H, s), 0.90 (3H, s), 0.96 (3H, s), 0.11 (3H, s),
1.21-2.02 (22H, m), 3.17 (1H, m) and 5.26(1H, s)

(Figure 37, page 196)

^{13}C - NMR (δ ppm, 75 MHz, CDCl_3): 15.3, 15.5, 17.1, 18.3, 22.9, 23.4, 23.6, 25.9, 27.2,
27.7, 28.1, 30.6, 32.4, 32.6, 33.0, 33.8, 37.1, 38.4,
38.7, 39.2, 40.9, 41.6, 45.8, 46.5, 47.6, 55.2, 79.0,
122.6, 143.6 and 183.6

(Figure 39, page 200)

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CHAPTER IV

RESULTS AND DISCUSSION

Chromatographic separation of the hexane and chloroform extracts of the stem of *Diospyros glandulosa* Lace led to the isolation of six chemical constituents. The identification of these compounds was based on analysis of their spectroscopic data and also confirmed by comparison with those values previously reported in the literature. The details can be discussed as follows.

1. Identification of Compound DG1

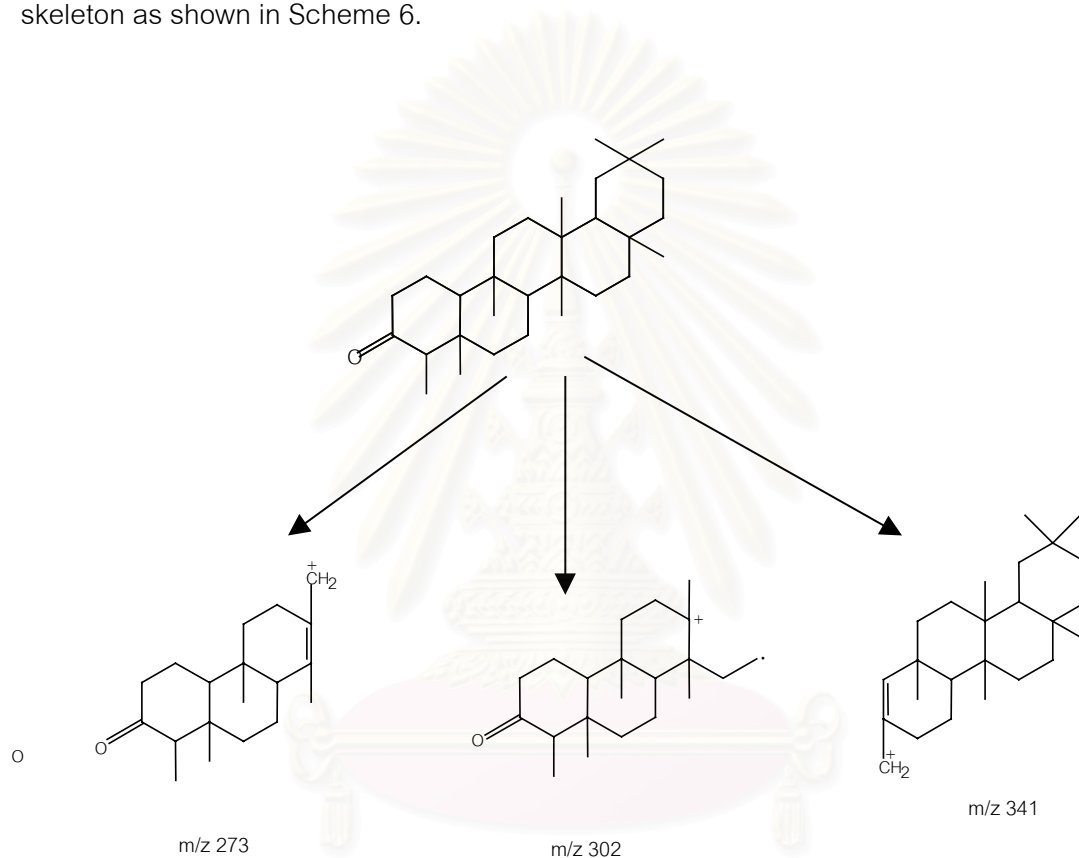
Compound DG1 was recrystallized as colorless needles from methanol (50.3 mg, 0.01% yield). The compound gave purple color to Liebermann-Burchard reagent, suggesting that it is a triterpenoid. Its EIMS (Figure 2) showed a molecular ion peak at m/z 426 which corresponded to the molecular formula of $C_{30}H_{50}O$. Its IR spectrum (Figure 3) displayed the keto absorption at 1714 cm^{-1} .

The ^1H and ^1H - ^1H COSY NMR spectra (Figures 4, 5) of DG1 displayed signals due to one secondary (δ 0.86 ppm; *d*) and seven tertiary methyls (δ 0.70, 0.85, 0.93, 0.98, 0.98, 1.03 and 1.16 ppm; *s*), suggestive of the friedelane skeleton. The ^{13}C -NMR spectrum of DG1 (Figure 6) showed 30 carbon signals. The DEPT and HETCOR experiments (Figures 7, 8) were employed to classify these signals into those of eight methyl carbons at δ 6.8, 14.6, 17.9, 18.6, 20.2, 31.8, 32.1, and 35.0 ppm, eleven methylene carbons at δ 18.2, 22.3, 30.5, 32.4, 32.8, 35.3, 35.6, 36.0, 39.2, 41.3 and 41.5 ppm, four methine carbons at δ 42.8, 53.1, 58.2 and 59.5 ppm, and seven quaternary carbons at δ 28.2, 30.0, 37.4, 38.3, 39.7, 42.1 and 213.2 ppm. The last signal indicated the presence of the keto group in the molecule of the compound.

The ^{13}C -NMR data of DG1 were found to be in full agreement with those values previously reported for friedelin (Akihisa, *et al.*, 1992), a friedelane-type triterpenoid with

3-keto substituent. Comparison of the ^{13}C -NMR assignment of DG1 and friedelin is shown in Table 14. The proton signals could then be assigned with the assistance of HETCOR experiment as shown in the same table.

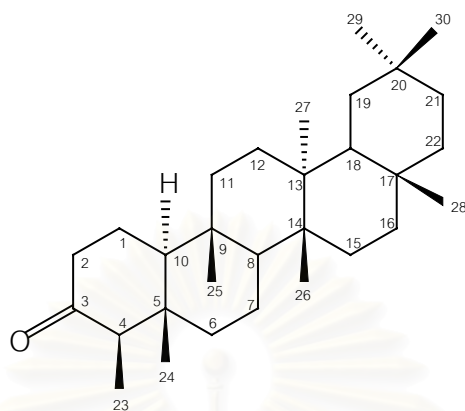
The EIMS also supported the structure of friedelin. The mass fragment peaks at m/z 273, 302 and 341 were the results of cleavage at different positions across the friedelin skeleton as shown in Scheme 6.



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Scheme 6. Mass fragmentation of compound DG1

Therefore, it was concluded that DG1 is friedelin, the structure of which is shown below.



Friedelin

Friedelin was previously isolated from several species of ebenaceous plant i.e. *Diospyros ferrea* (Tiwari, *et al.*, 1979), *D. eriantha* (Chen, *et al.*, 1992) and *D. maritima* (Higa, *et al.*, 1998). This compound has been reported as possessing cytotoxic activity (Zheng, 1994).

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Table 15. ^1H and ^{13}C -NMR assignments of compound DG1 (in CDCl_3) and the reported ^{13}C -NMR assignments of friedelin (in CDCl_3)

Position	Compound DG1		Friedelin
	δ H (ppm)	δ C (ppm)	δ C (ppm)
1	1.67 (m), 1.96 (m)	22.3	22.3
2	2.23 (m), 2.39 (m)	41.5	41.5
3	-	213.2	213.2
4	2.23(m)	58.2	58.2
5	-	42.1	42.1
6	1.27 (m), 1.74 (m)	41.3	41.3
7	1.33 (m), 1.45 (m)	18.2	18.2
8	1.37 (m)	53.1	53.1
9	-	37.4	37.4
10	1.50 (2H, m)	59.5	59.4
11	1.20-1.60 (m)	35.6	35.6
12	1.20-1.60 (m)	30.5	30.5
13	-	39.7	39.7
14	-	38.3	38.3
15	1.20-1.60 (m)	32.4	32.4
16	1.20-1.60 (m)	36.0	36.0
17	-	30.0	30.0
18	1.53 (m)	42.8	42.8
19	1.20-1.60 (m)	35.3	35.3
20	-	28.2	28.1
21	1.20-1.60 (m)	32.8	32.7
22	0.94 (m), 1.48 (m)	39.2	39.2
23	0.86 (d, $J= 6.0$ Hz)	6.8	6.8
24	0.70 (s)	14.6	14.6
25	0.85 (s)	17.9	17.9
26	0.98 (s)	20.2	20.2
27	1.03 (s)	18.6	18.6
28	1.16 (s)	32.1	32.1
29	0.93 (s)	35.0	35.0
30	0.98 (s)	31.8	31.8

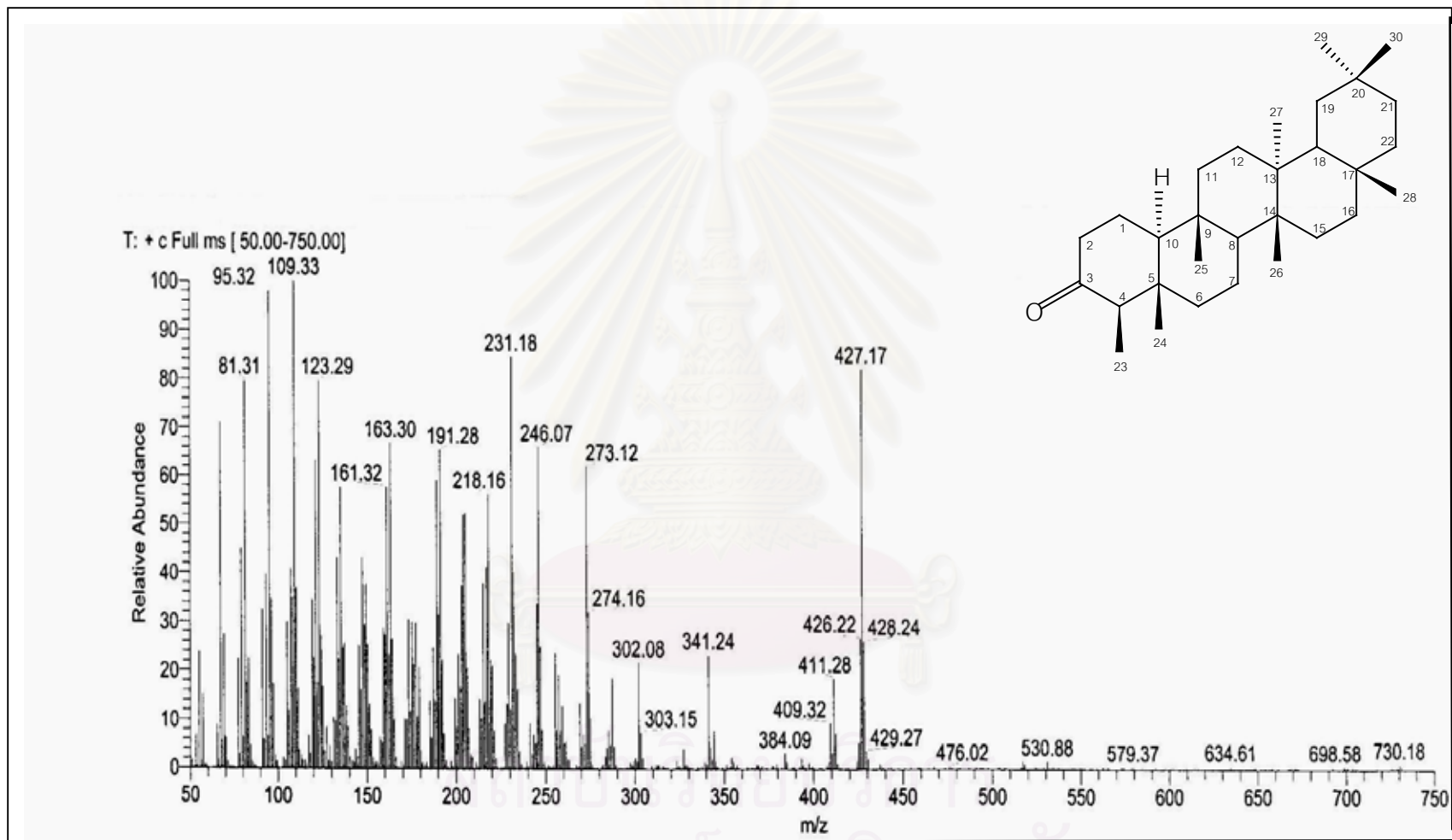


Figure 2. EIMS of compound DG1

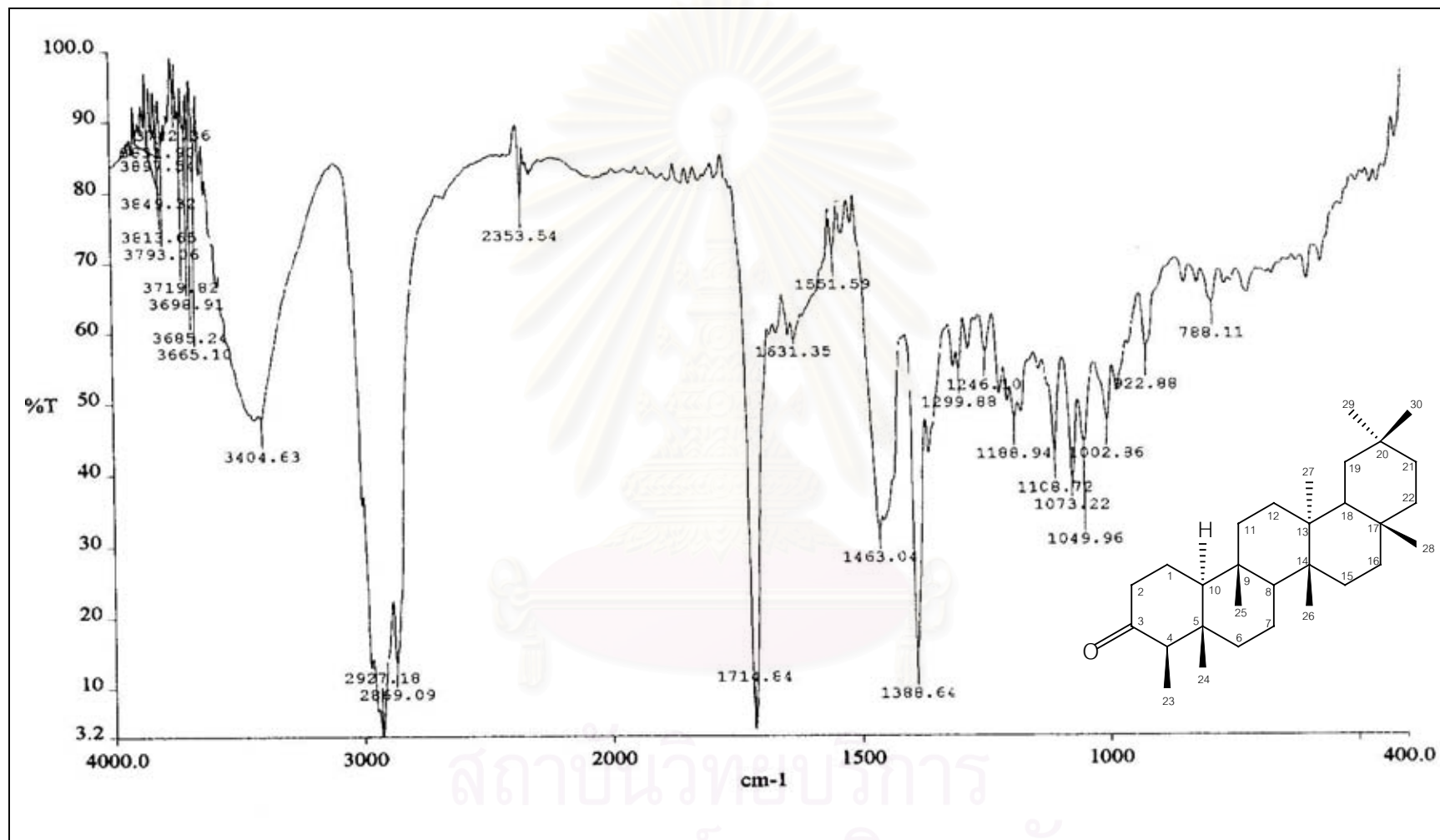


Figure 3. IR spectrum of compound DG1

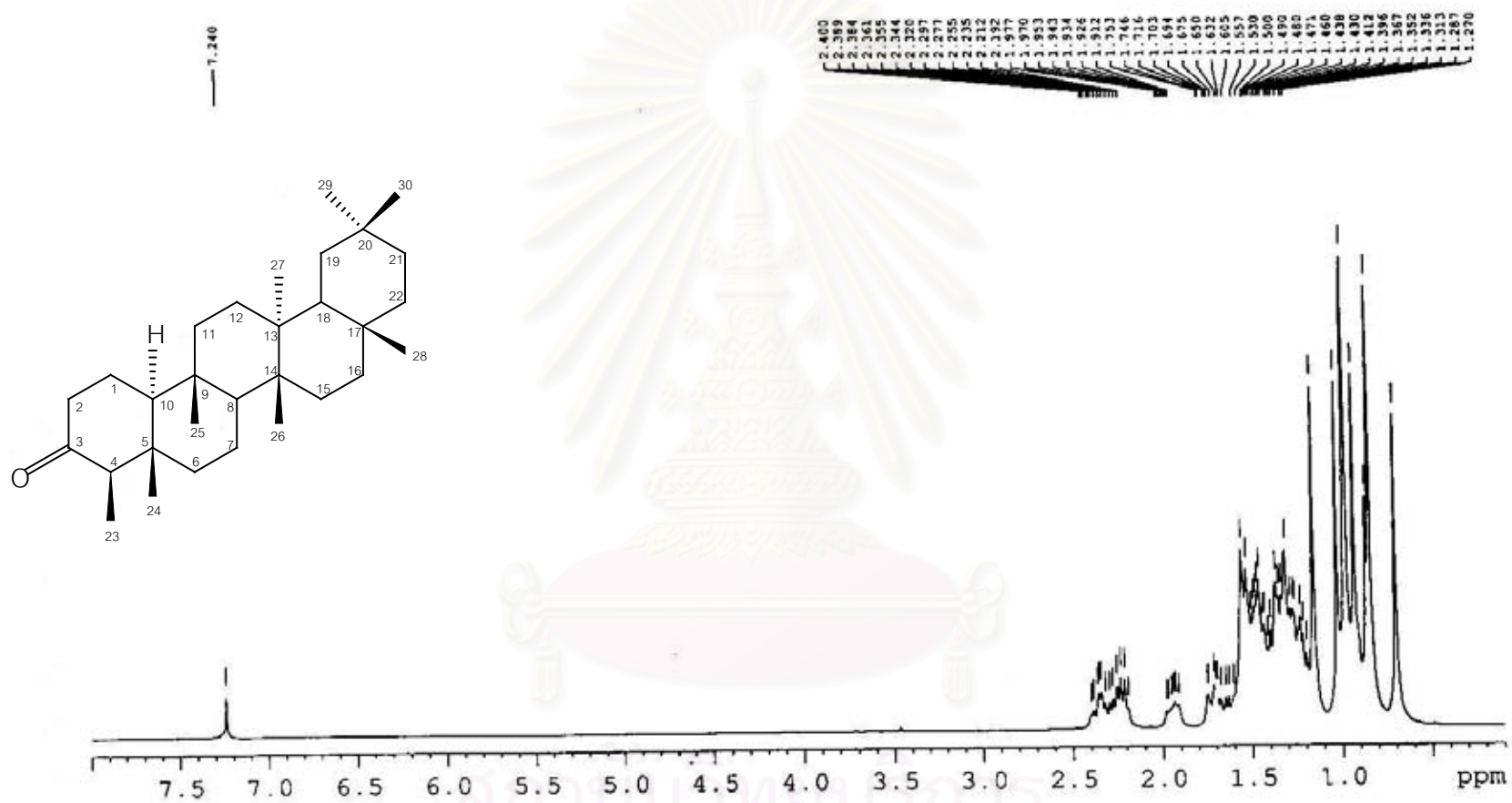


Figure 4a. The 300 MHz $^1\text{H-NMR}$ spectrum of compound DG1 (in CDCl_3)

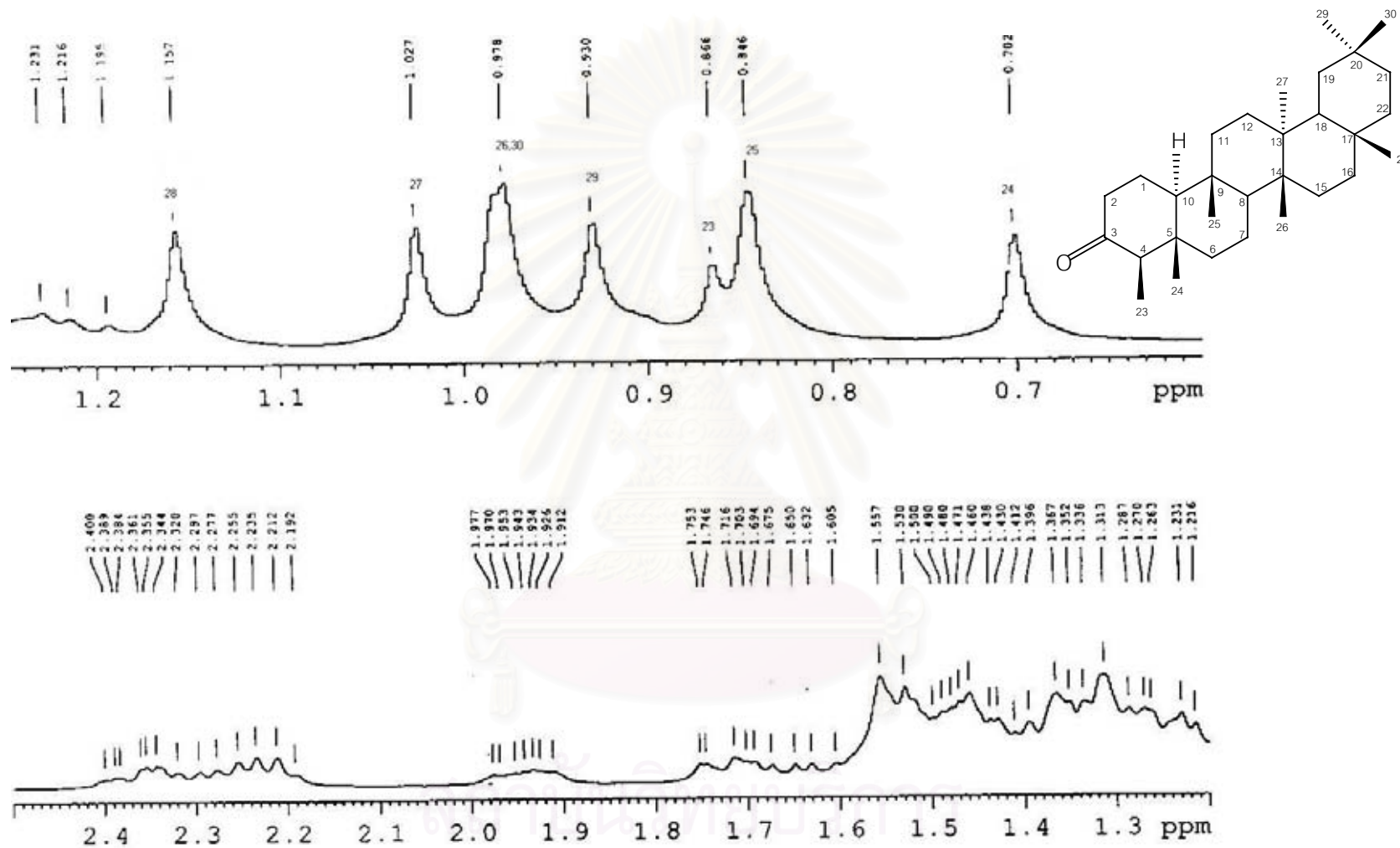


Figure 4b. The 300 MHz ¹H-NMR spectrum of compound DG1 (expanded)

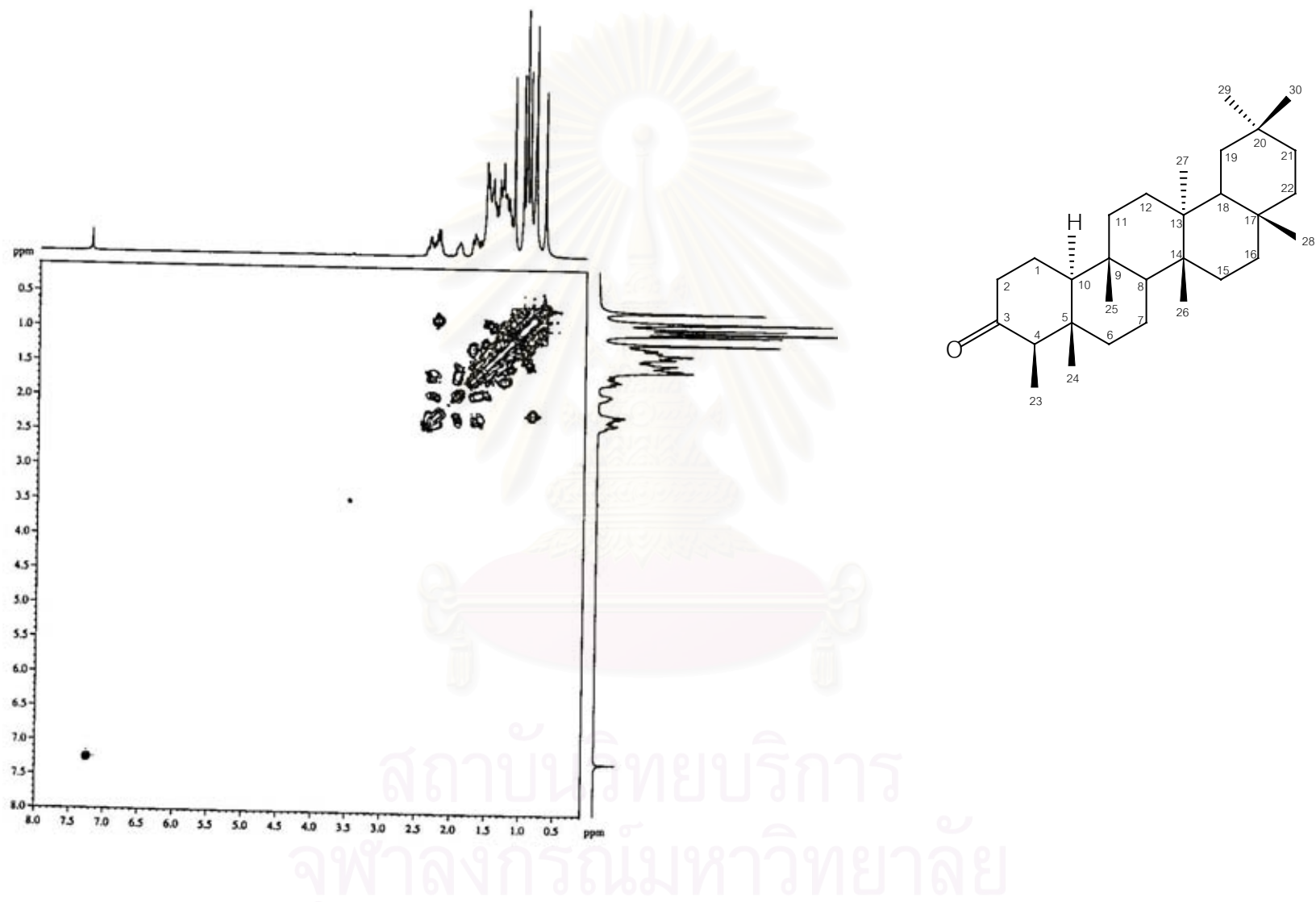


Figure 5a. The 300 MHz ^1H - ^1H COSY spectrum of compound DG1 (in CDCl_3)

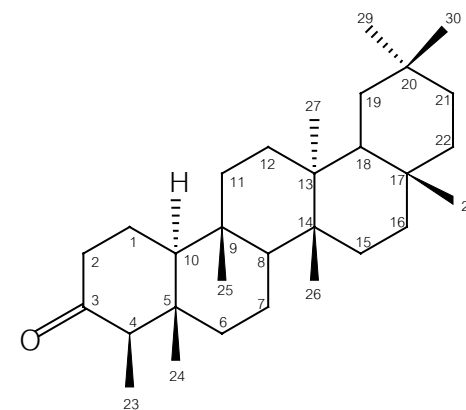
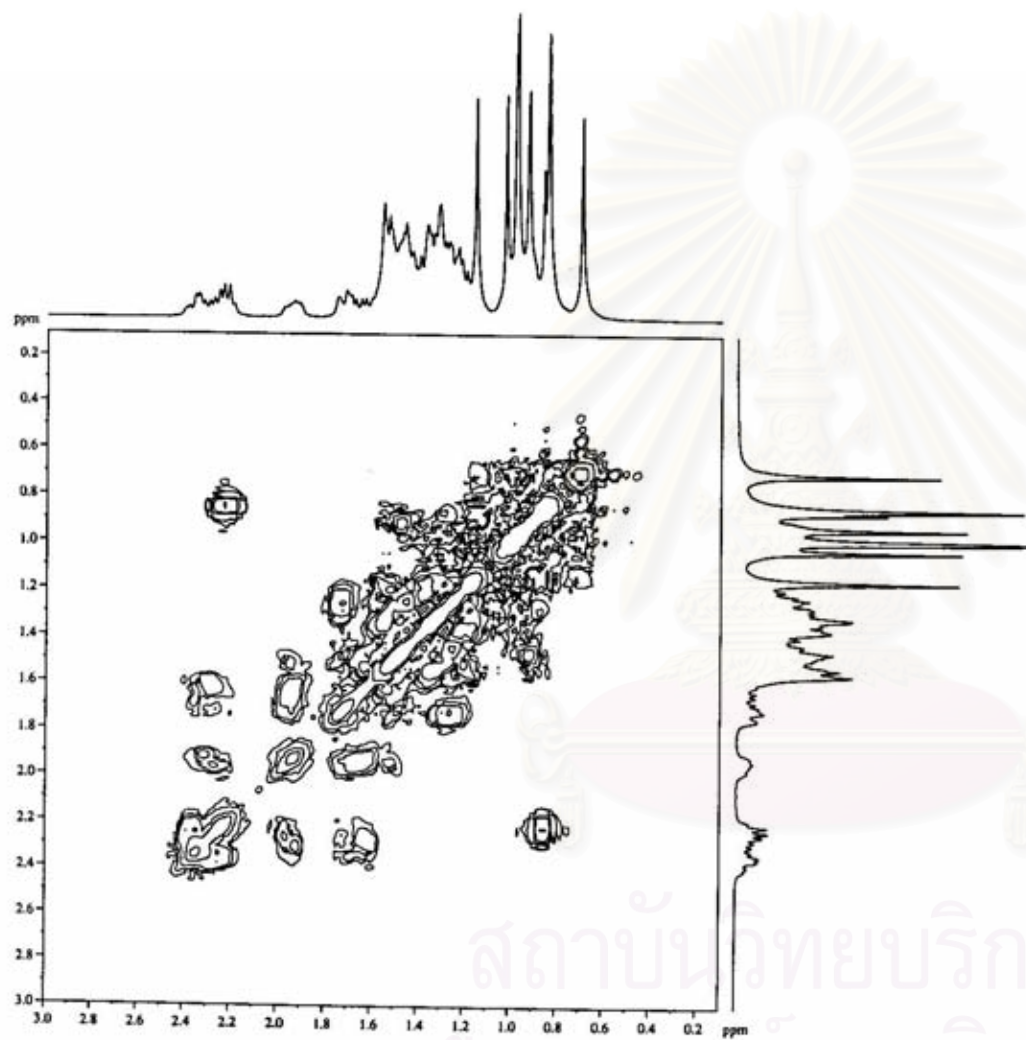


Figure 5b. The 300 MHz ¹H-¹H COSY spectrum of compound DG1 (expanded)

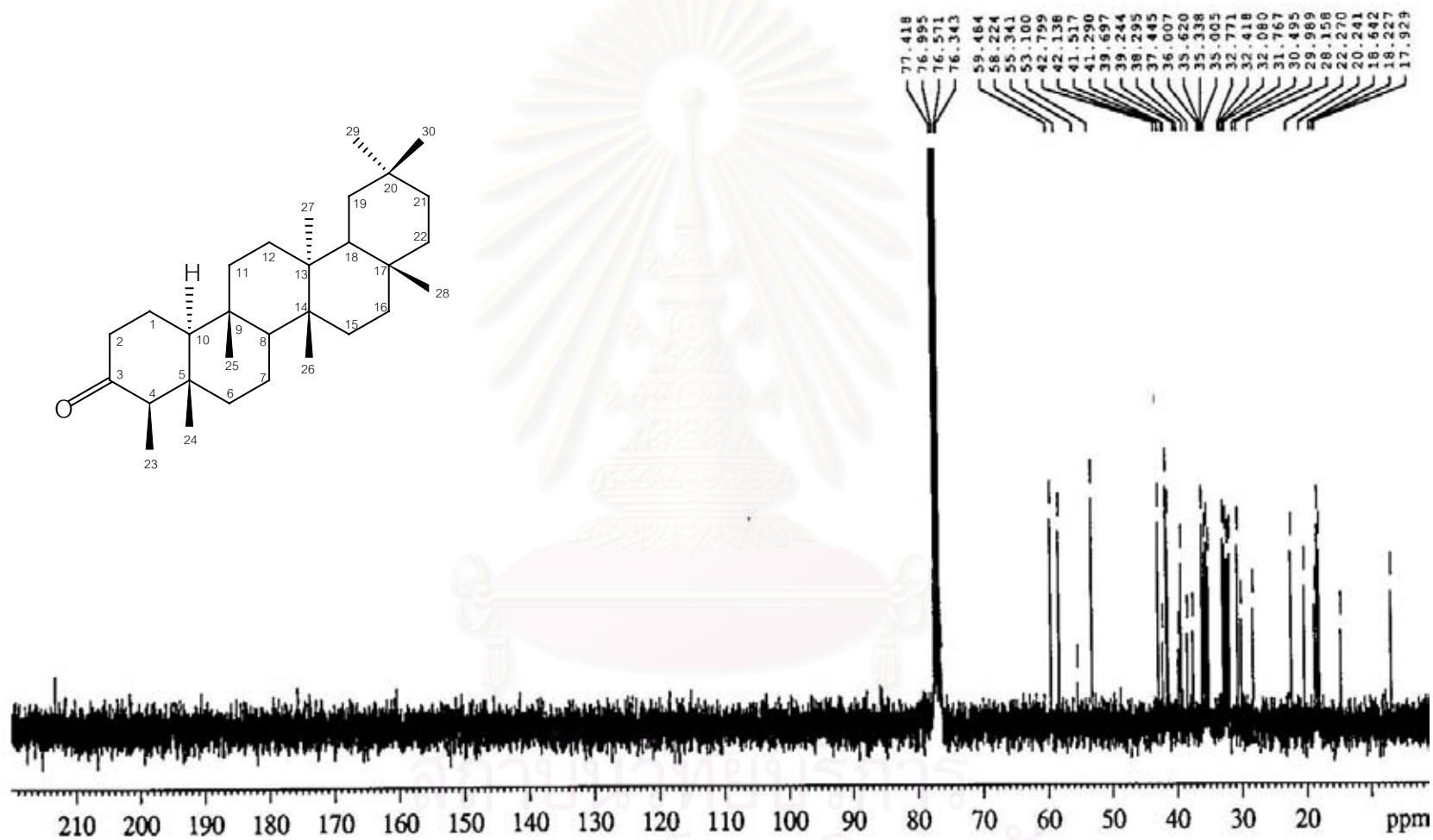


Figure 6a. The 75 MHz ¹³C-NMR spectrum of compound DG1 (in CDCl₃)

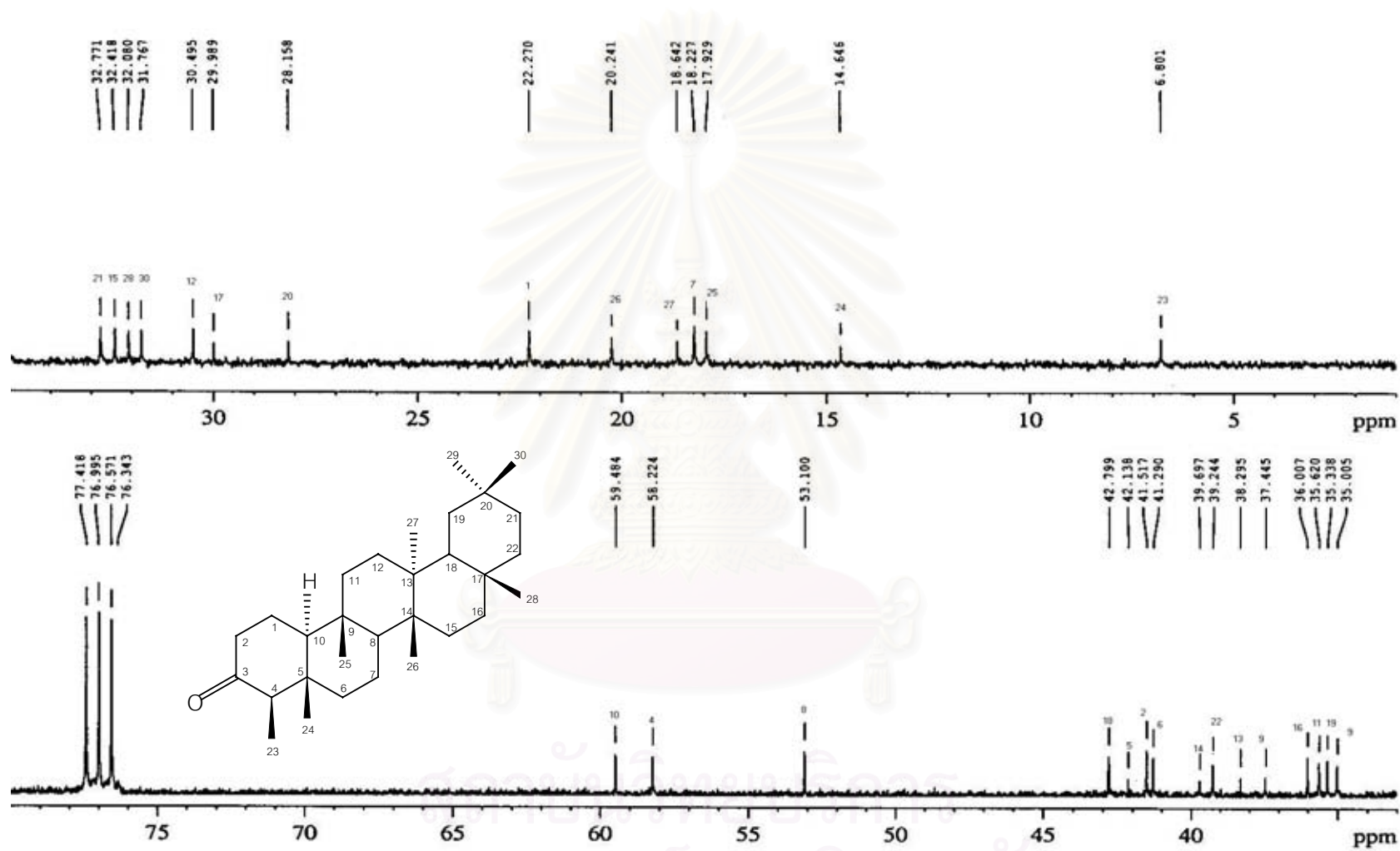


Figure 6b. The 75 MHz ^{13}C -NMR spectrum of compound DG1 (expanded)

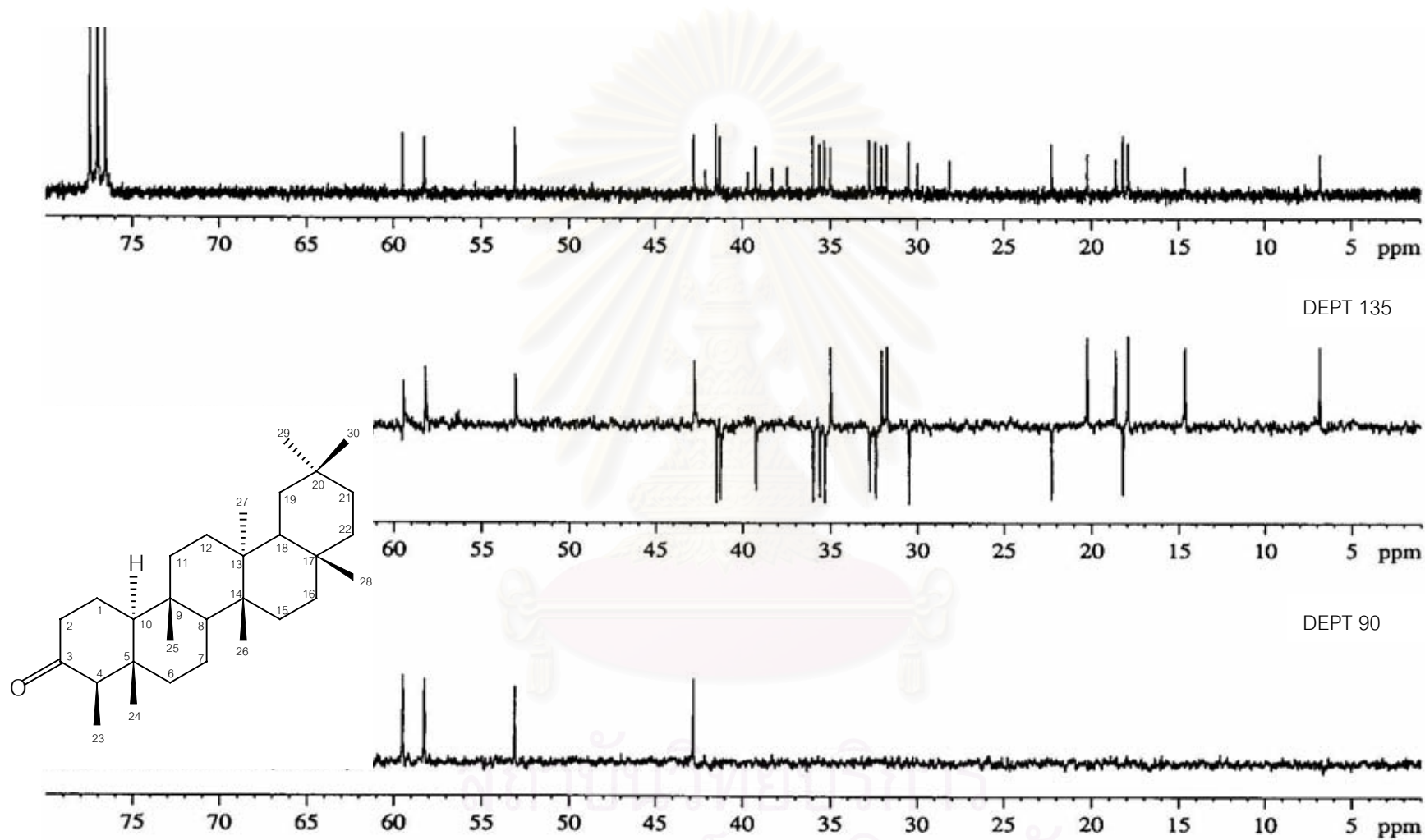


Figure 7. The 75 MHz ^{13}C -DEPT NMR spectrum of compound DG1 (in CDCl_3)

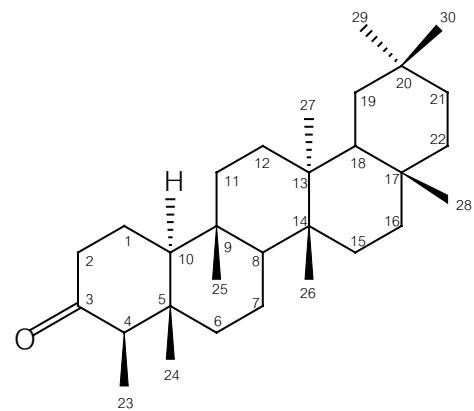
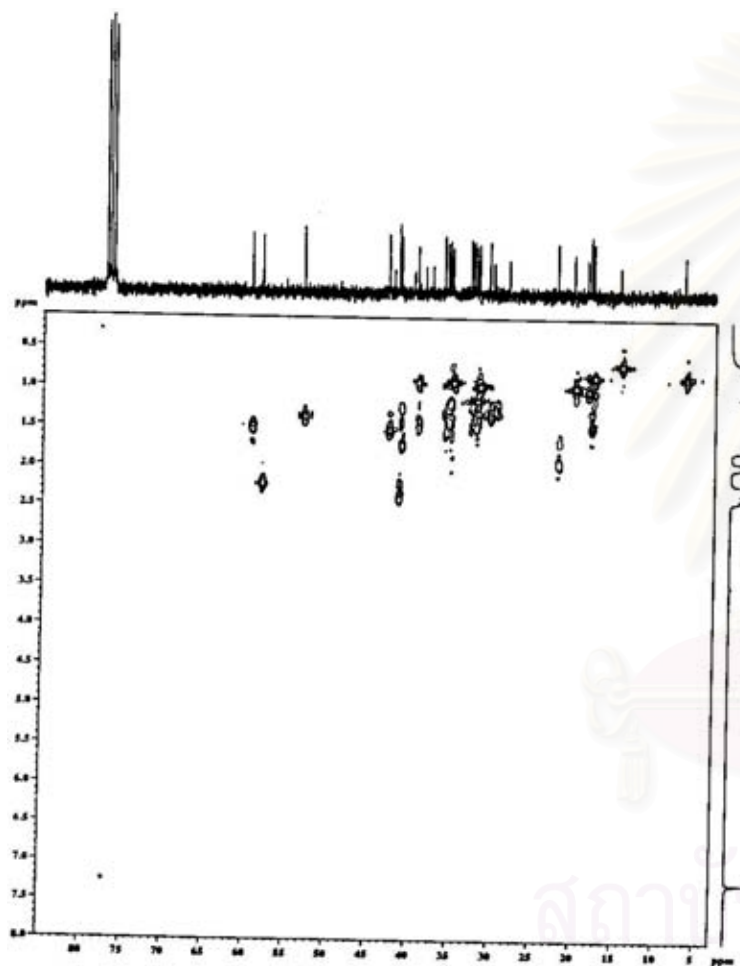


Figure 8a. The 75 MHz ^1H - ^{13}C HETCOR NMR spectrum of compound DG1 (in CDCl_3)

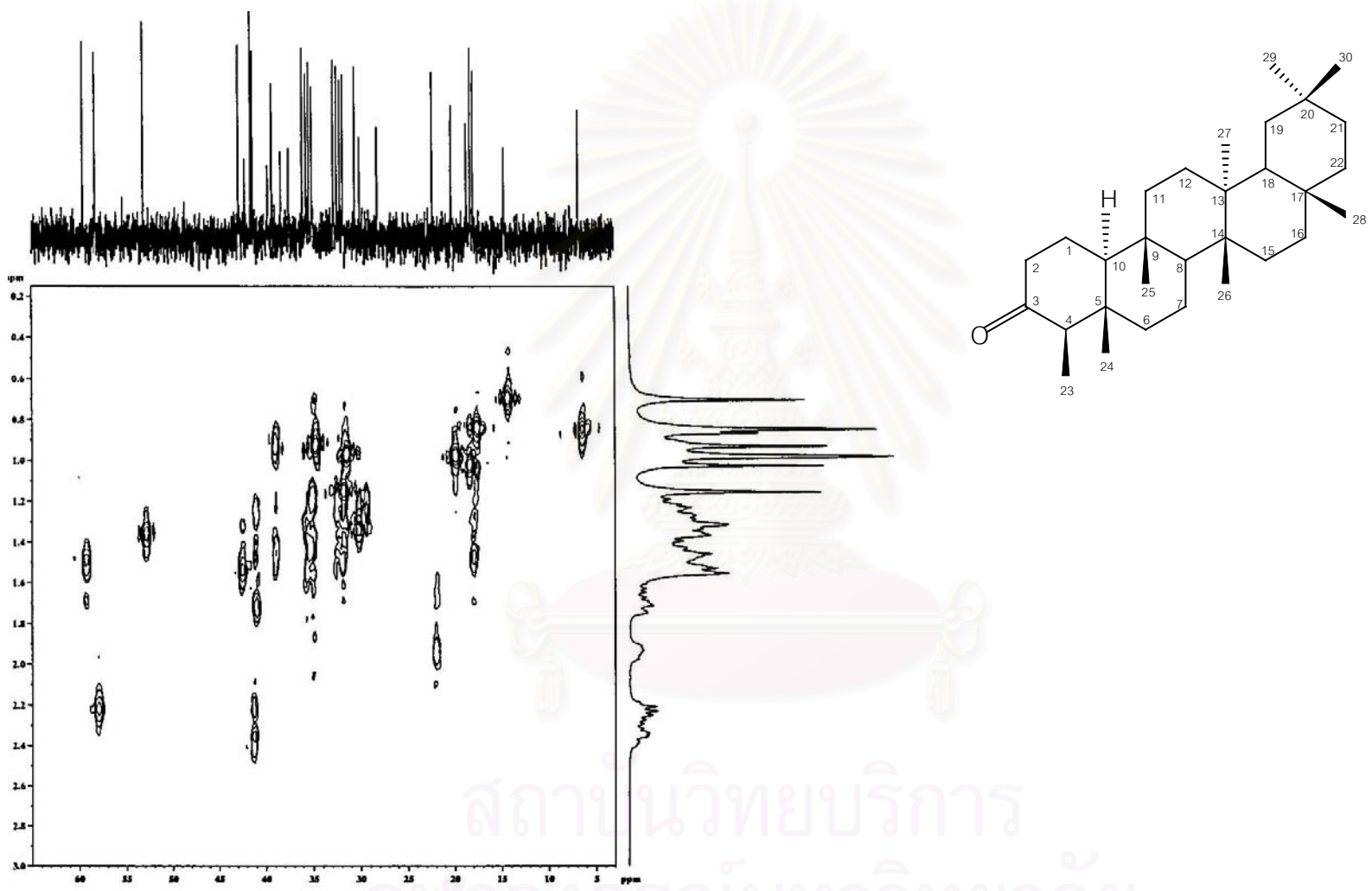


Figure 8b. The 75 MHz ^1H - ^{13}C HETCOR NMR spectrum of compound DG1 (expanded)

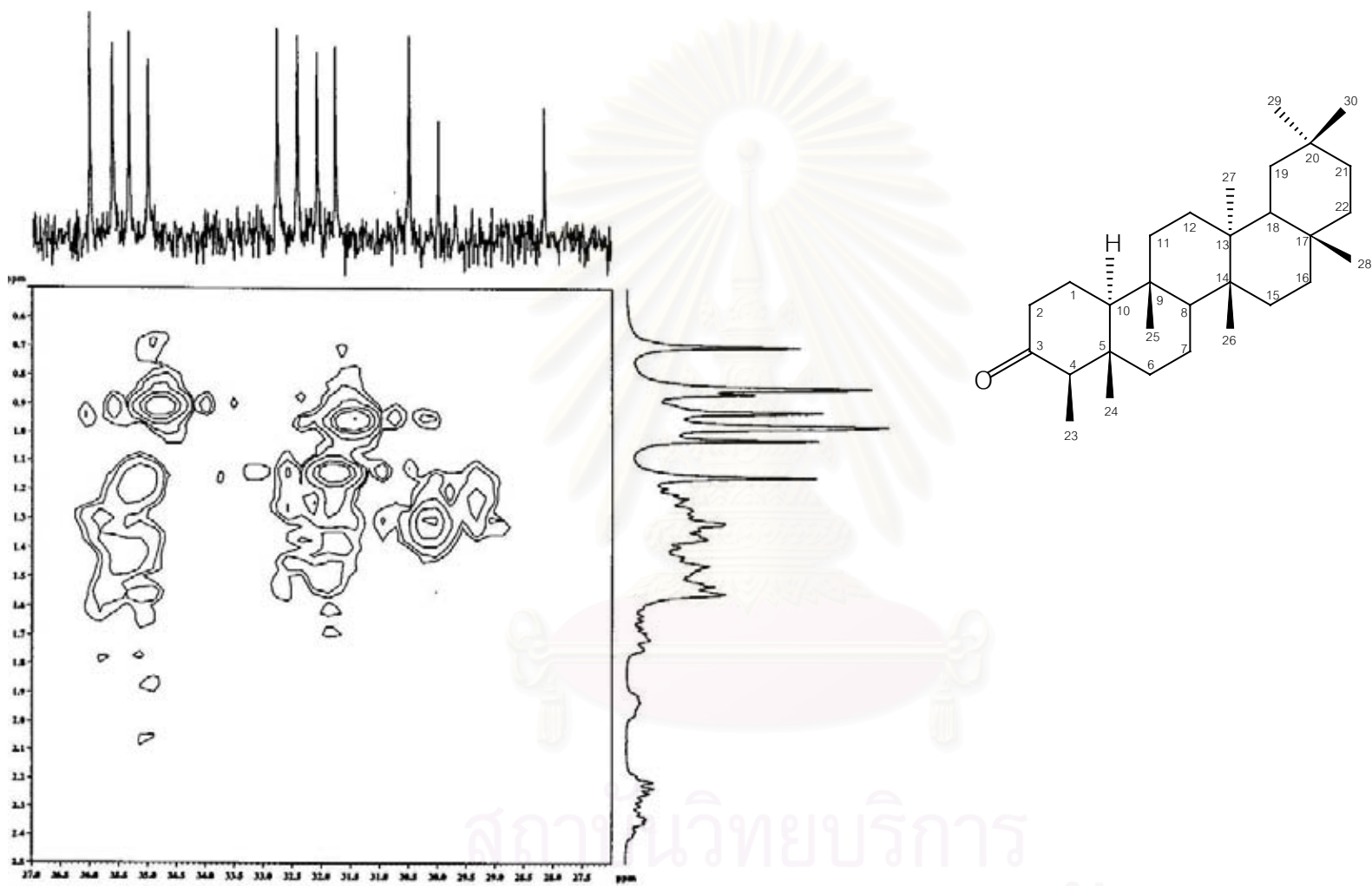


Figure 8c. The 75 MHz ^1H - ^{13}C HETCORR NMR spectrum of compound DG1 (expanded)

2. Identification of Compound DG2

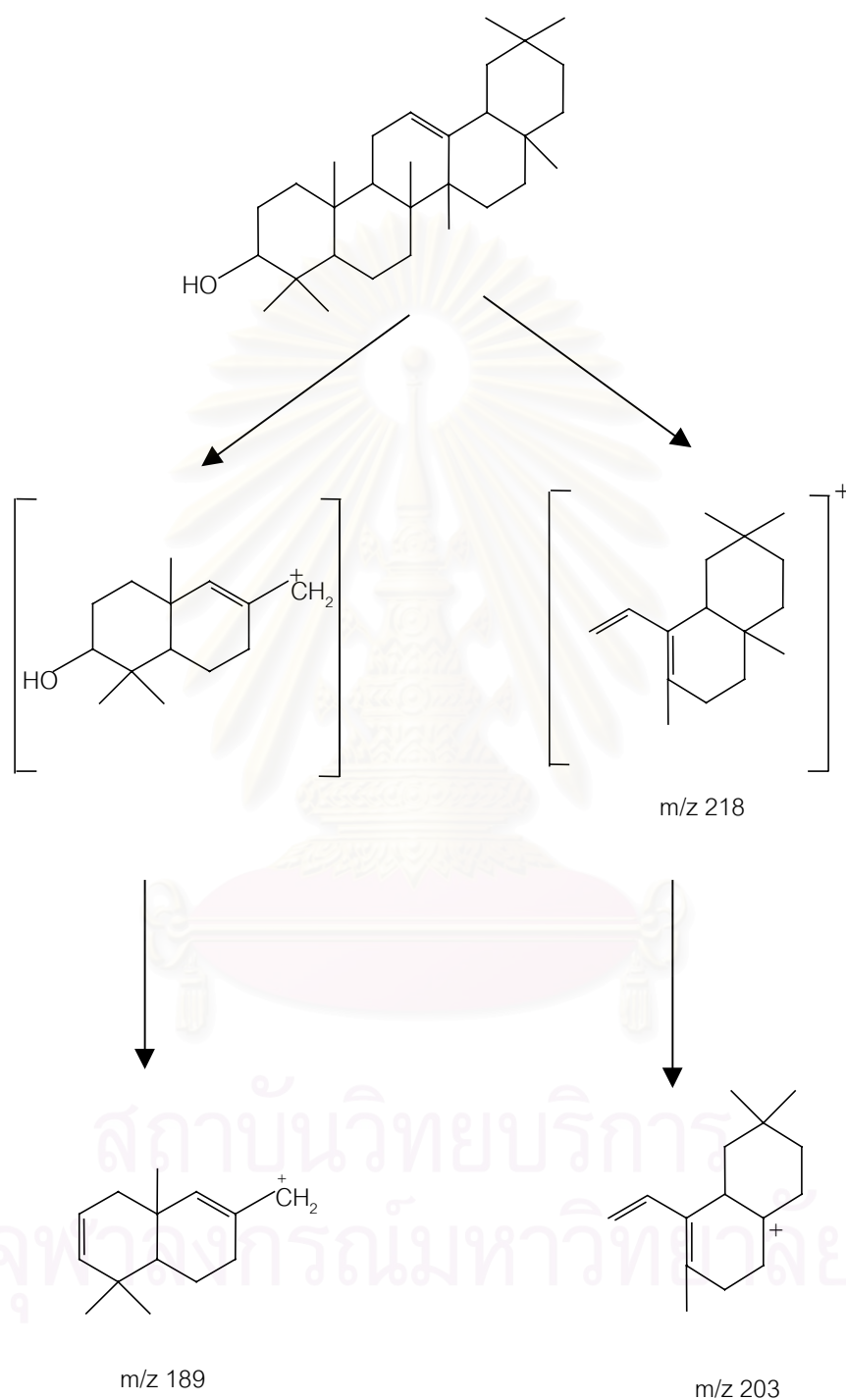
Compound DG2 was recrystallized as colorless needles from methanol (20.3 mg, 0.004% yield). The compound gave purple color to Liebermann-Burchard reagent, suggesting that it is a triterpenoid. Its EIMS (Figure 9) showed molecular ion peak at m/z 426 which corresponded to the molecular formula of $C_{30}H_{50}O$. The base peak at m/z 218, produced through retro-Diels-Alder fragmentation, is the characteristic feature of a C-12 unsaturated oleanane or ursane triterpenoid containing no substituents in both ring D and E (Ogunkoya, 1981). The further loss of one methyl group produced the mass fragment peak at m/z 203, and the loss of water from the other retro-Diels-Alder fragment led to the peak at m/z 189 (Scheme 7). The IR spectrum (Figure 10) showed absorption band at 3282 cm^{-1} , suggesting the presence of a hydroxyl substituent.

The $^1\text{H-NMR}$ and $^1\text{H-}^1\text{H COSY}$ spectra (Figures 11,12) of DG2 showed eight singlets of tertiary methyls (δ 0.77, 0.81, 0.85, 0.85, 0.92, 0.95, 0.98 and 1.12 ppm), suggestive of the oleanane skeleton. The proton signal at δ 3.20 (*dd*, $J=5.0, 10.7\text{Hz}$) ppm confirmed the presence of a hydroxyl substituent. The most downfield signal at δ 5.17 (*br. t*) represents H-12 of a C-12 unsaturated triterpenoid.

The $^{13}\text{C-NMR}$ spectrum of DG2 (Figure 13) showed 30 carbon signals. The DEPT and HETCOR experiments (Figures 14, 15) exhibited the signals of eight methyl carbons at δ 15.5, 15.6, 16.8, 23.7, 26.0, 28.1, 28.4 and 33.3 ppm, ten methylene carbons at δ 18.4, 23.6, 26.1, 26.9, 27.2, 32.5, 34.7, 37.1, 38.6 and 46.8 ppm, five methine carbons at δ 47.2, 47.6, 55.2, 79.0 and 121.7 ppm and seven quaternary carbons at δ 31.1, 32.6, 36.9, 38.8, 39.8, 41.7 and 145.2 ppm.

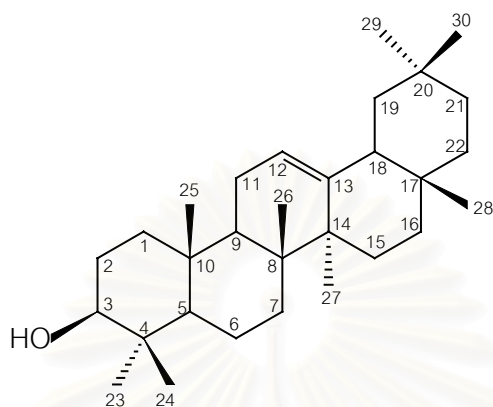
According to all information mentioned above, DG2 was proposed as a C-12 unsaturated triterpenoid of the oleanane type. The downfield carbon signals at δ 121.7 and δ 145.2 ppm represent the characteristic double bond between C-12 and C-13 in the oleanane skeleton. Comparison of the $^{13}\text{C-NMR}$ data of DG2 with those previously reported for β -amyrin (Mahato and Kundu, 1994) a known olea-12-ene indicated the structures of

both compounds to be indicated. Comparison of the ^{13}C -NMR assignment of DG2 and β -amyrin, together with the ^1H -NMR assignment of DG2, are shown in Table 16.



Scheme 7. The mass fragmentation of compound DG2

Therefore, DG2 was identified as β -amyrin, the structure of which is shown below.



β -Amyrin was previously isolated from several species of ebenceous plants, i.e. *Diospyros peregrina* (Tandon, *et al.*, 1974), *D. morrisiana* (Yan, *et al.*, 1989) and *D. melanoxylon* (Mallavadhani, *et al.*, 2001). The compound has been reported as possessing anti-inflammatory (Akihisa, *et al.*, 1996) and cytotoxic (Yan, *et al.*, 1989) activities.

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Table 16. ^1H and ^{13}C -NMR assignments of compound DG2 (in CDCl_3) and the reported ^{13}C -NMR assignment of β -Amyrin (in CDCl_3)

position	Compound DG2		β -Amyrin
	δ H (ppm)	δ C (ppm)	δ C (ppm)
1	-	38.6	38.7
2	-	27.2	27.3
3	3.20 (dd, $J=5.0, 10.7$ Hz)	79.0	79.0
4	-	38.8	38.8
5	-	55.2	55.3
6	-	18.4	18.5
7	-	32.5	32.8
8	-	39.8	38.8
9	-	47.6	47.7
10	-	36.9	37.6
11	-	23.6	23.6
12	5.17 (br. t)	121.7	121.8
13	-	145.2	145.1
14	-	41.7	41.8
15	-	26.1	26.2
16	-	26.9	27.0
17	-	32.6	32.5
18	-	47.2	47.4
19	-	46.8	46.9
20	-	31.1	31.1
21	-	34.7	34.8
22	-	37.1	37.2
23	0.98 (s)	28.1	28.2
24	0.92 (s)	15.5	15.5
25	0.77 (s)	15.6	15.6
26	0.95 (s)	16.8	16.9
27	1.12 (s)	26.0	26.0
28	0.81 (s)	28.4	28.4
29	0.85 (s)	33.3	33.3
30	0.85 (s)	23.7	23.7

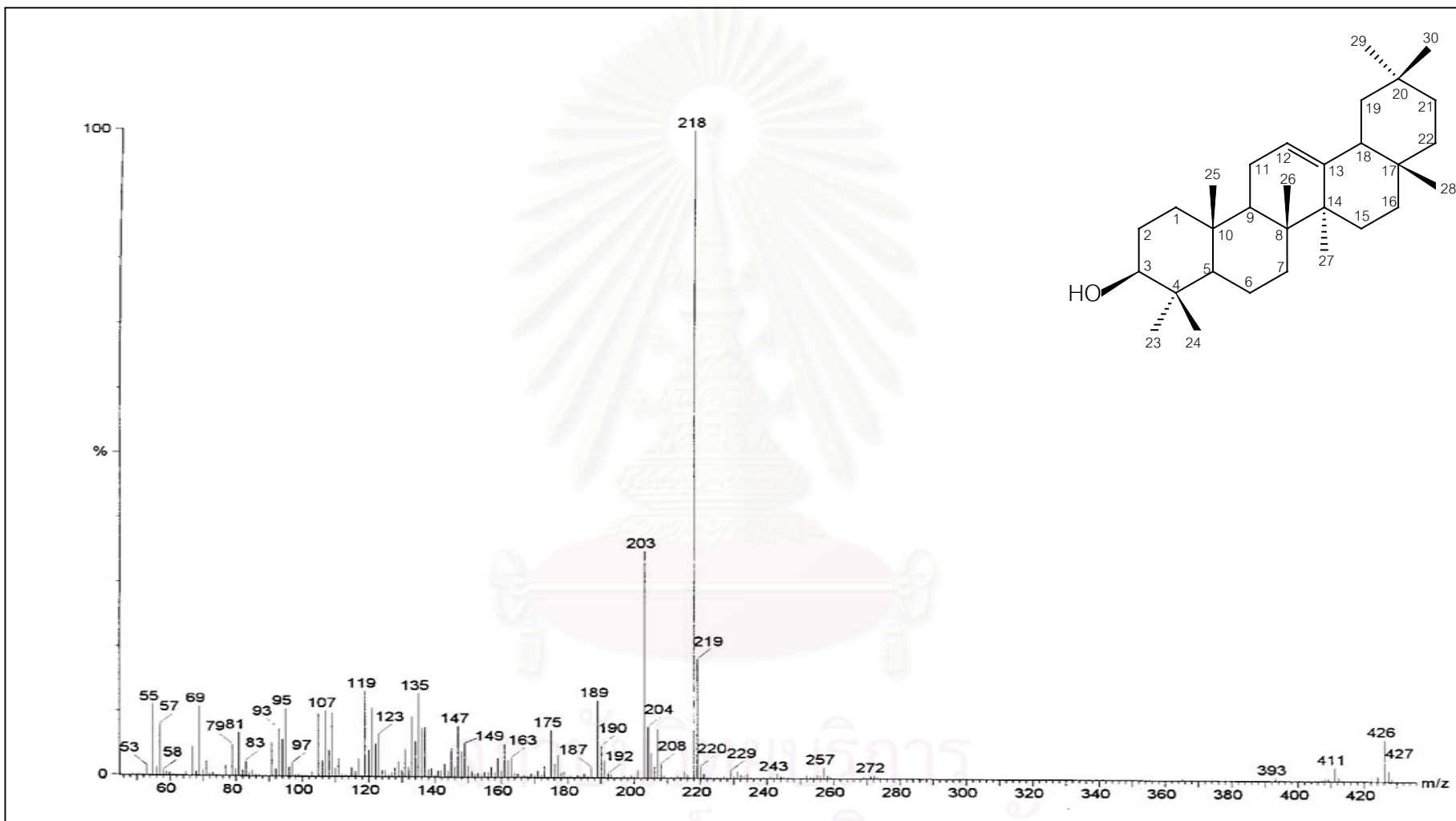


Figure 9. EIMS of compound DG2

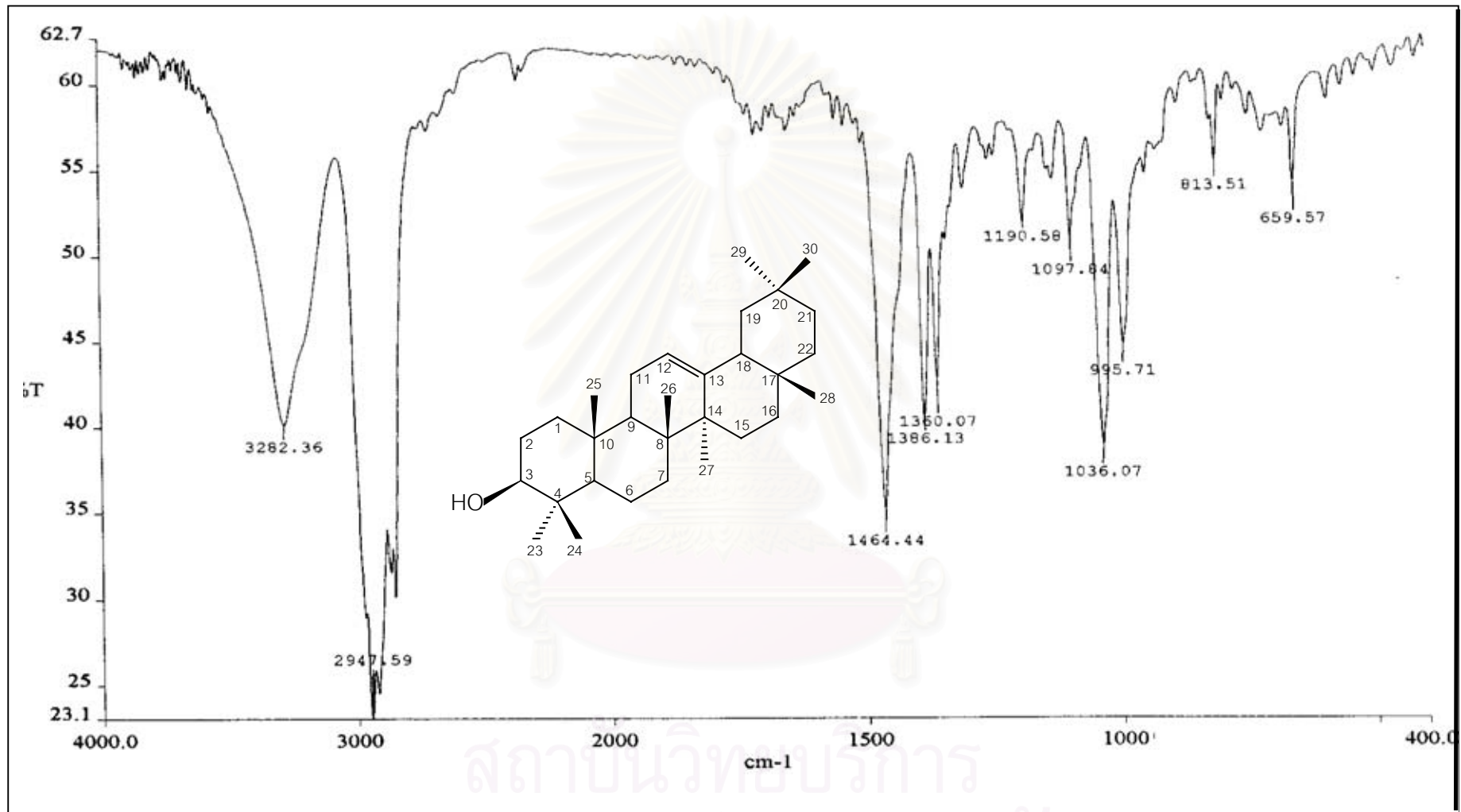


Figure 10. IR spectrum of compound DG2

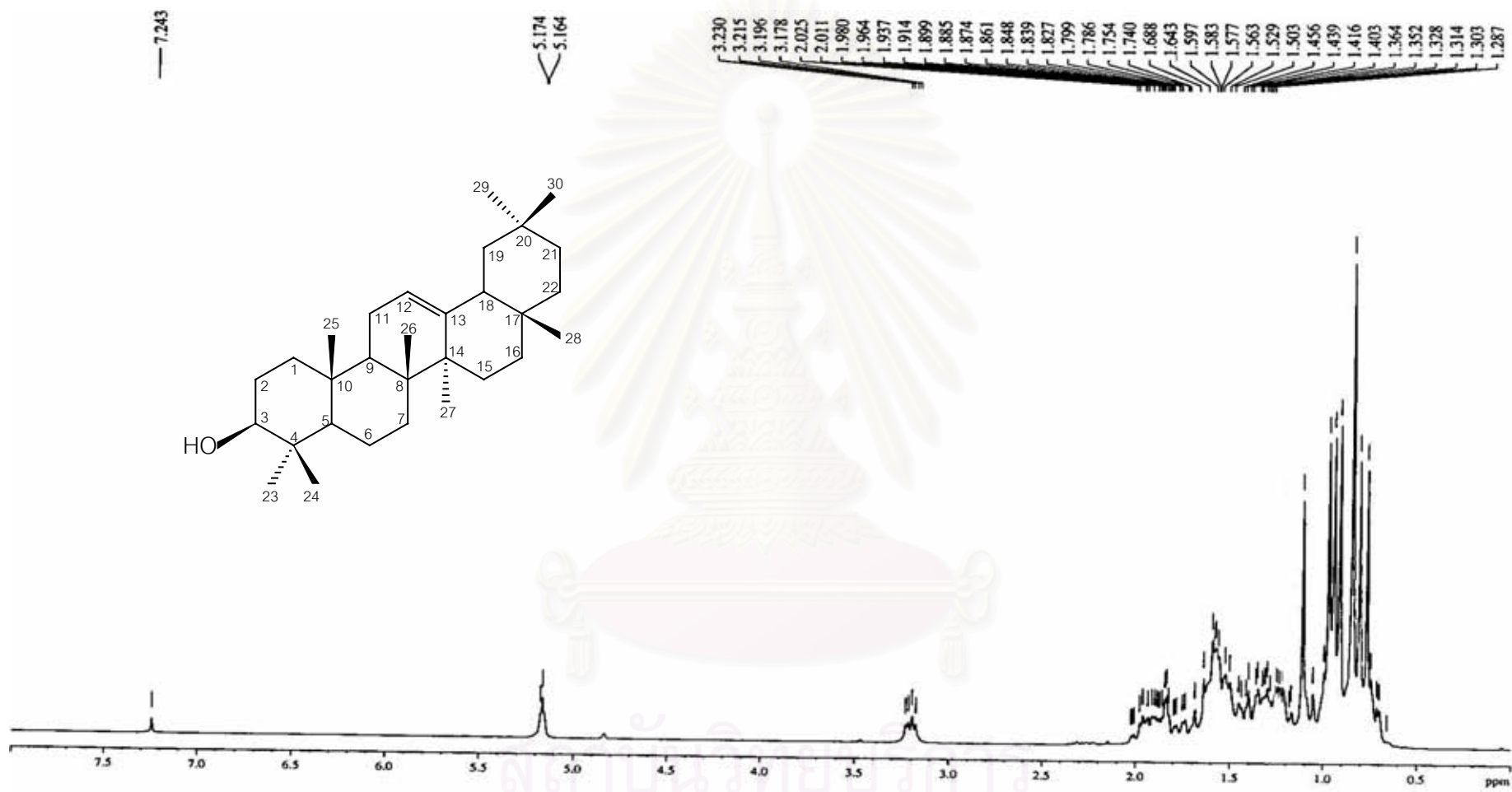


Figure 11a. The 300 MHz ¹H-NMR spectrum of compound DG2 (in CDCl₃)

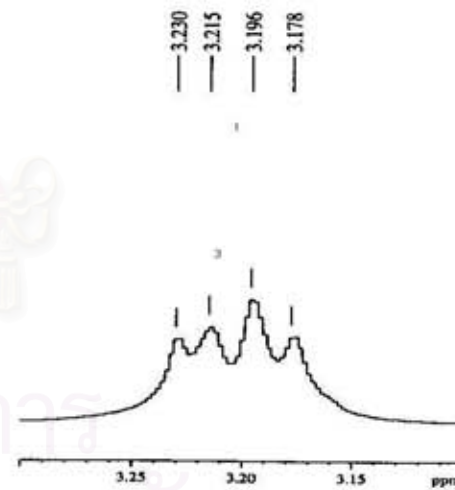
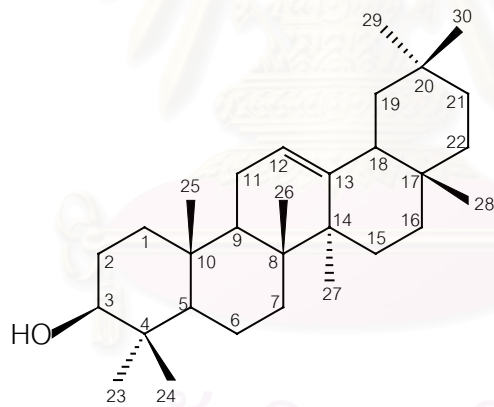
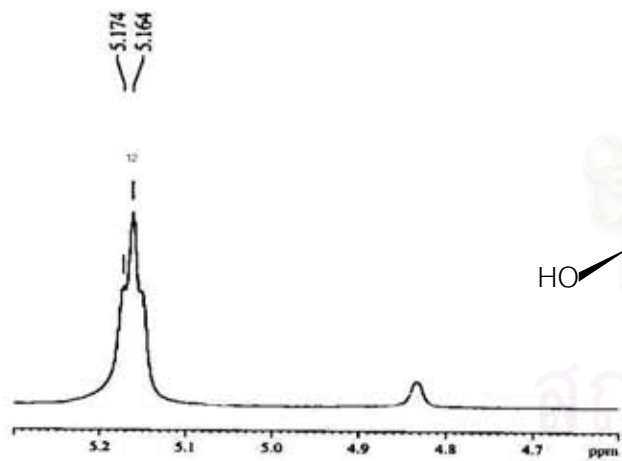
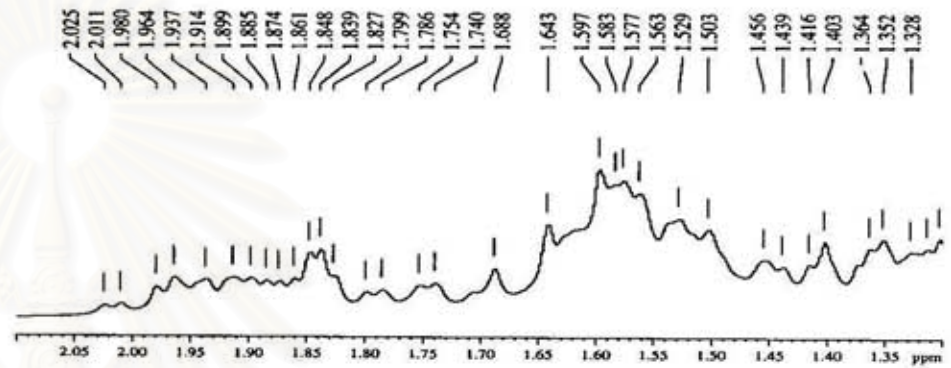
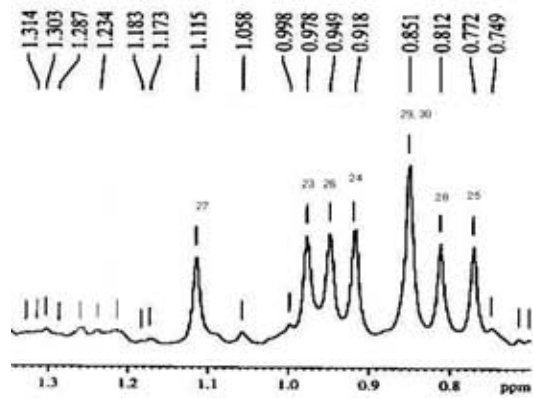


Figure 11b. The 300 MHz ^1H -NMR spectrum of compound DG2 (expanded)

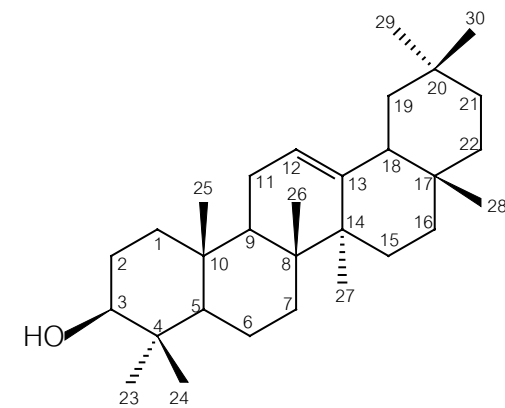
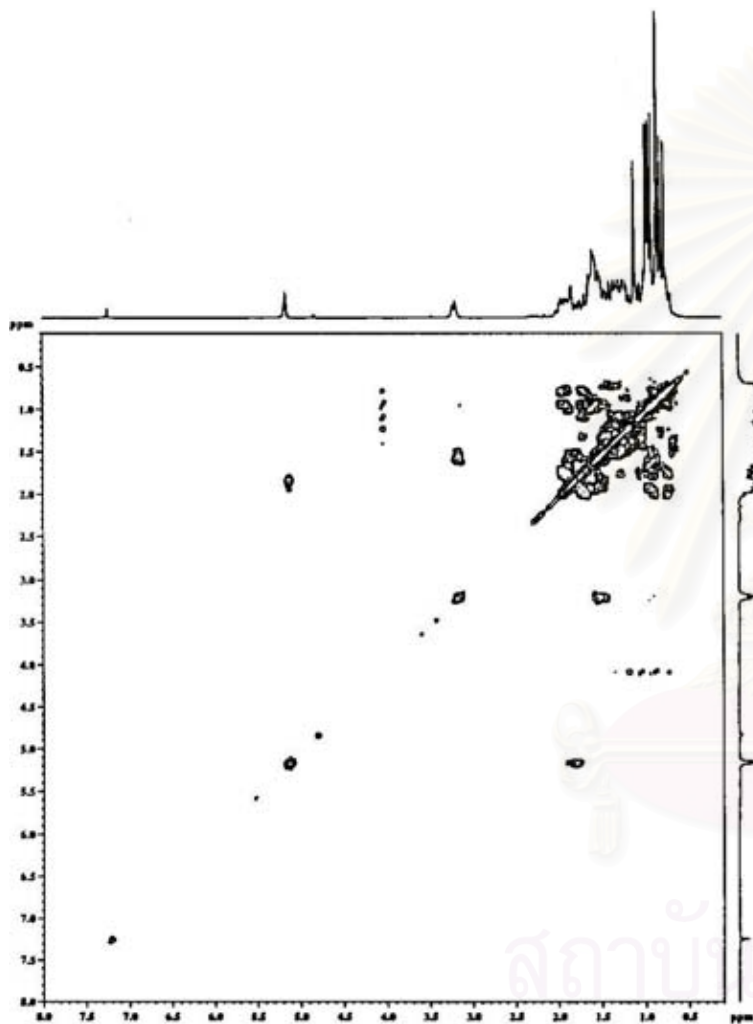


Figure 12a. The 300 MHz ^1H - ^1H COSY spectrum of compound DG2 (in CDCl_3)

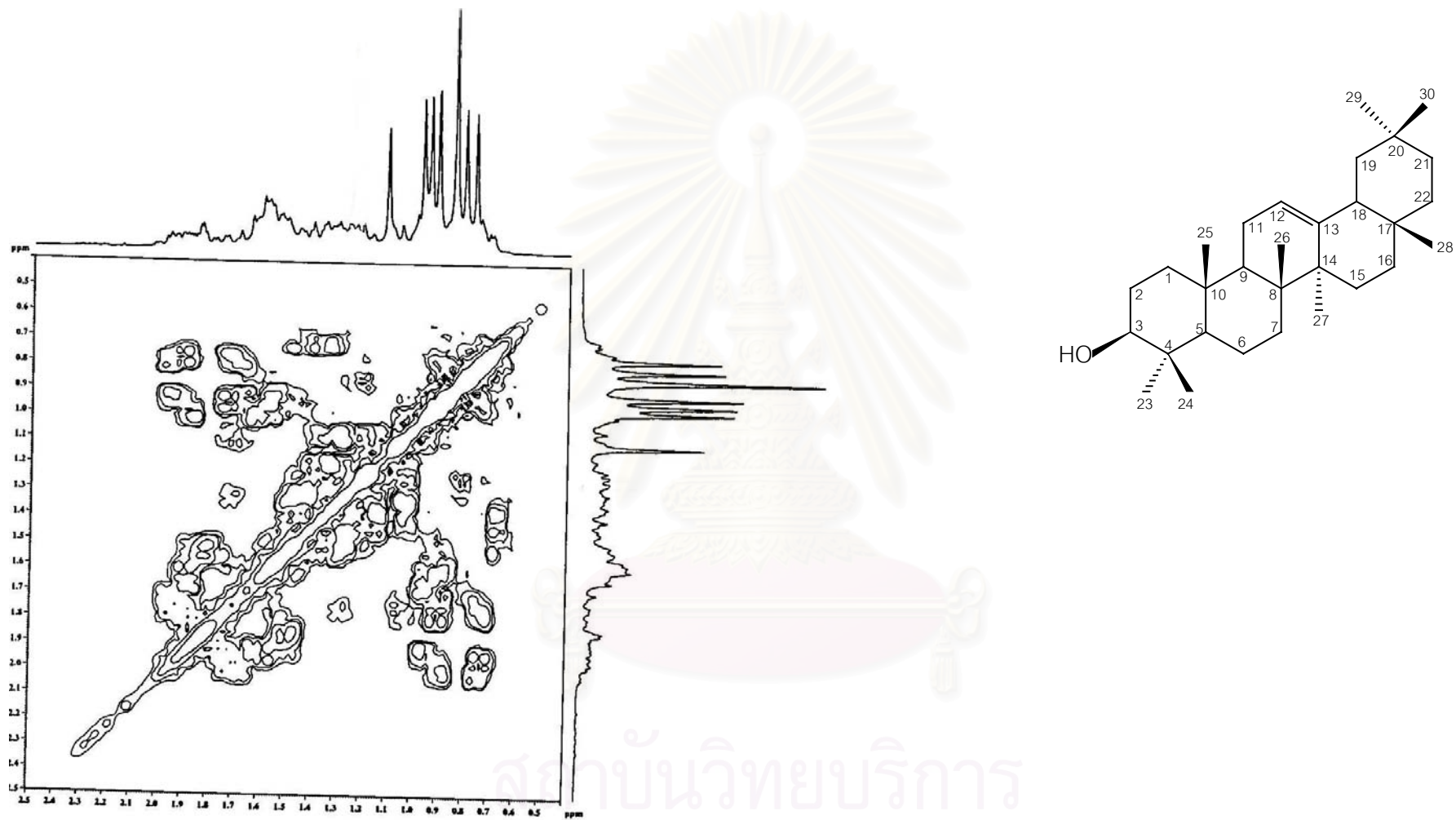


Figure 12b. The 300 MHz ^1H - ^1H COSY spectrum of compound DG2 (expanded)

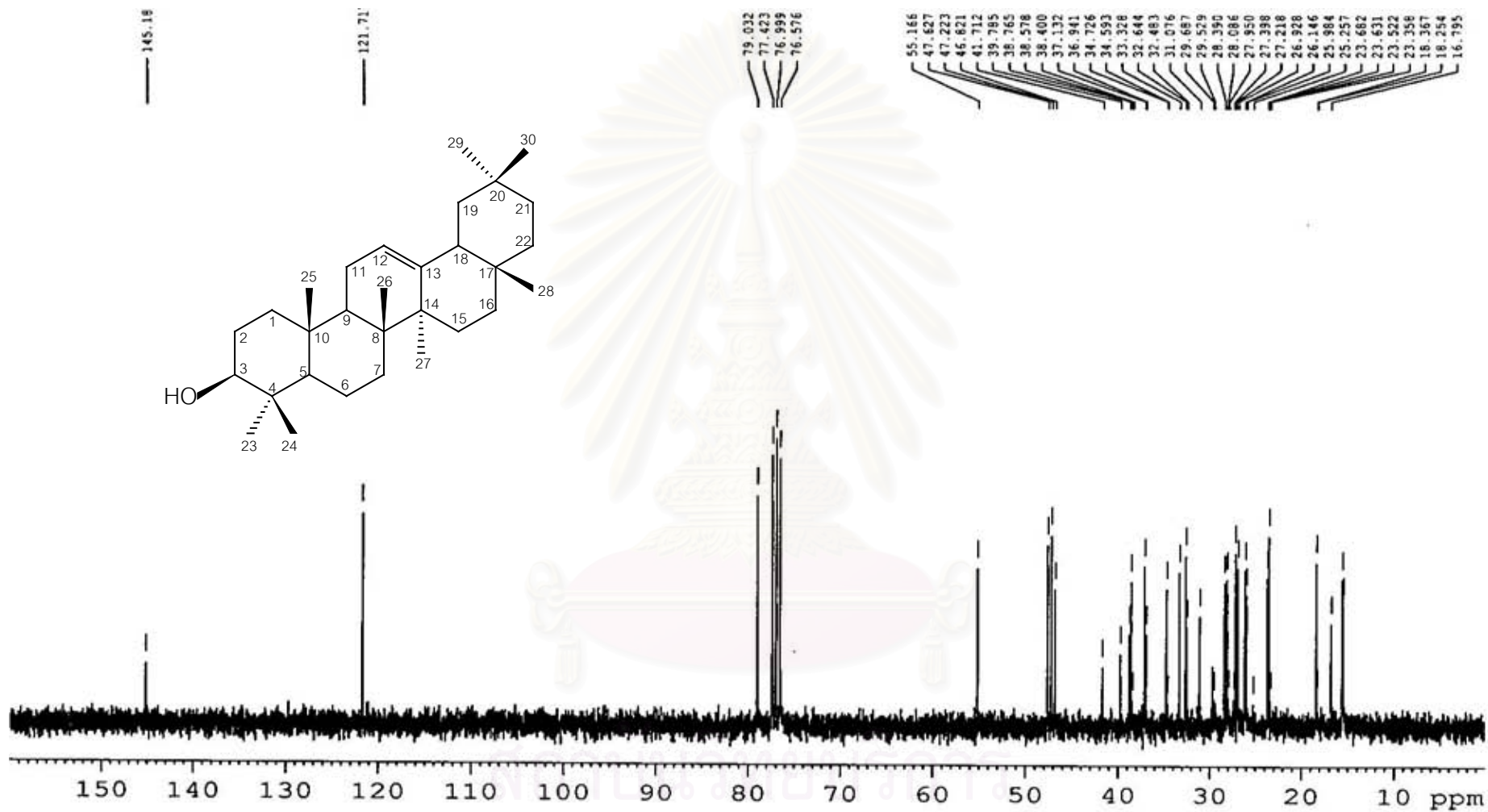


Figure 13a. The 75 MHz ^{13}C -NMR spectrum of compound DG2 (in CDCl_3)

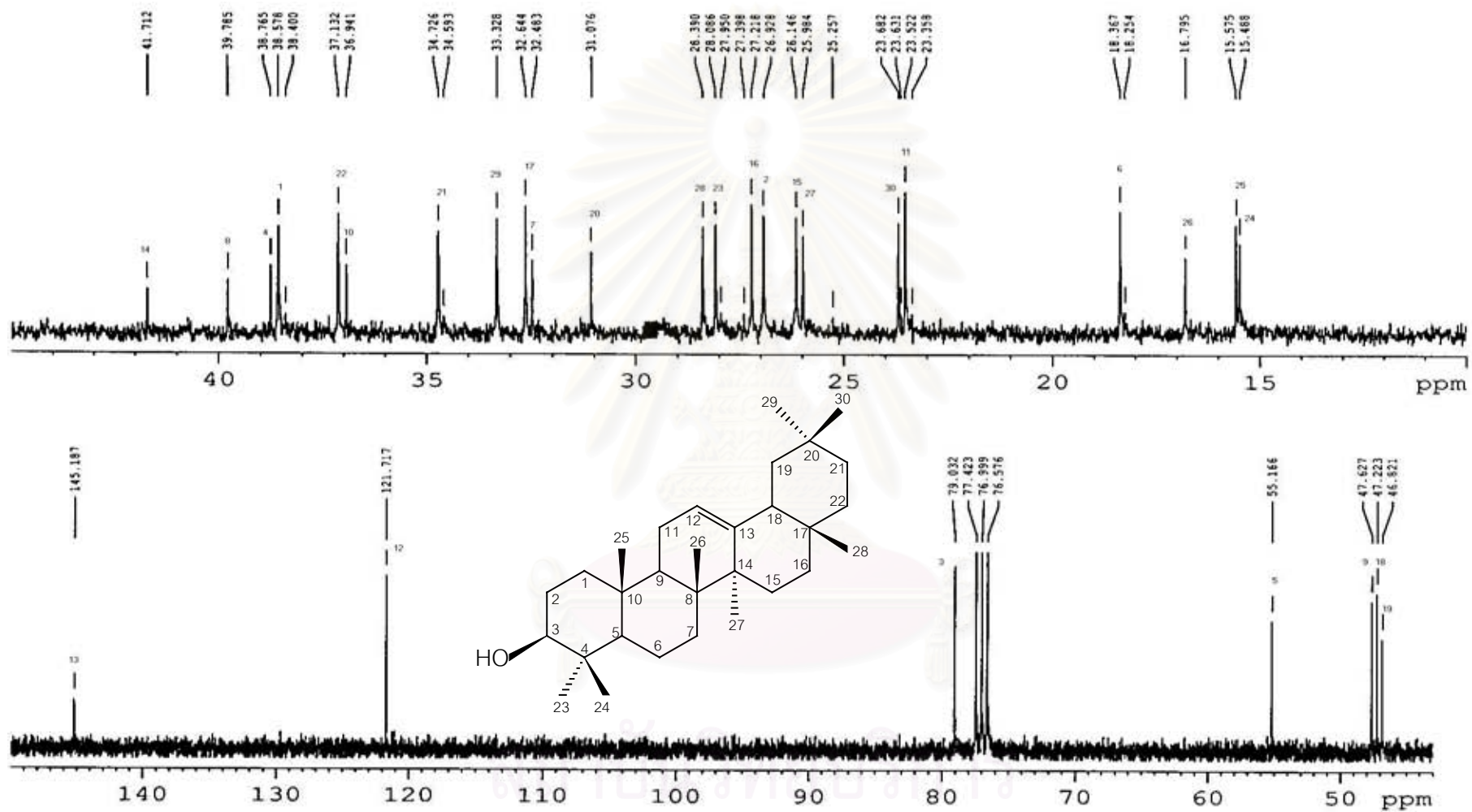


Figure 13b. The 75 MHz ^{13}C -NMR spectrum of compound DG2 (expanded)

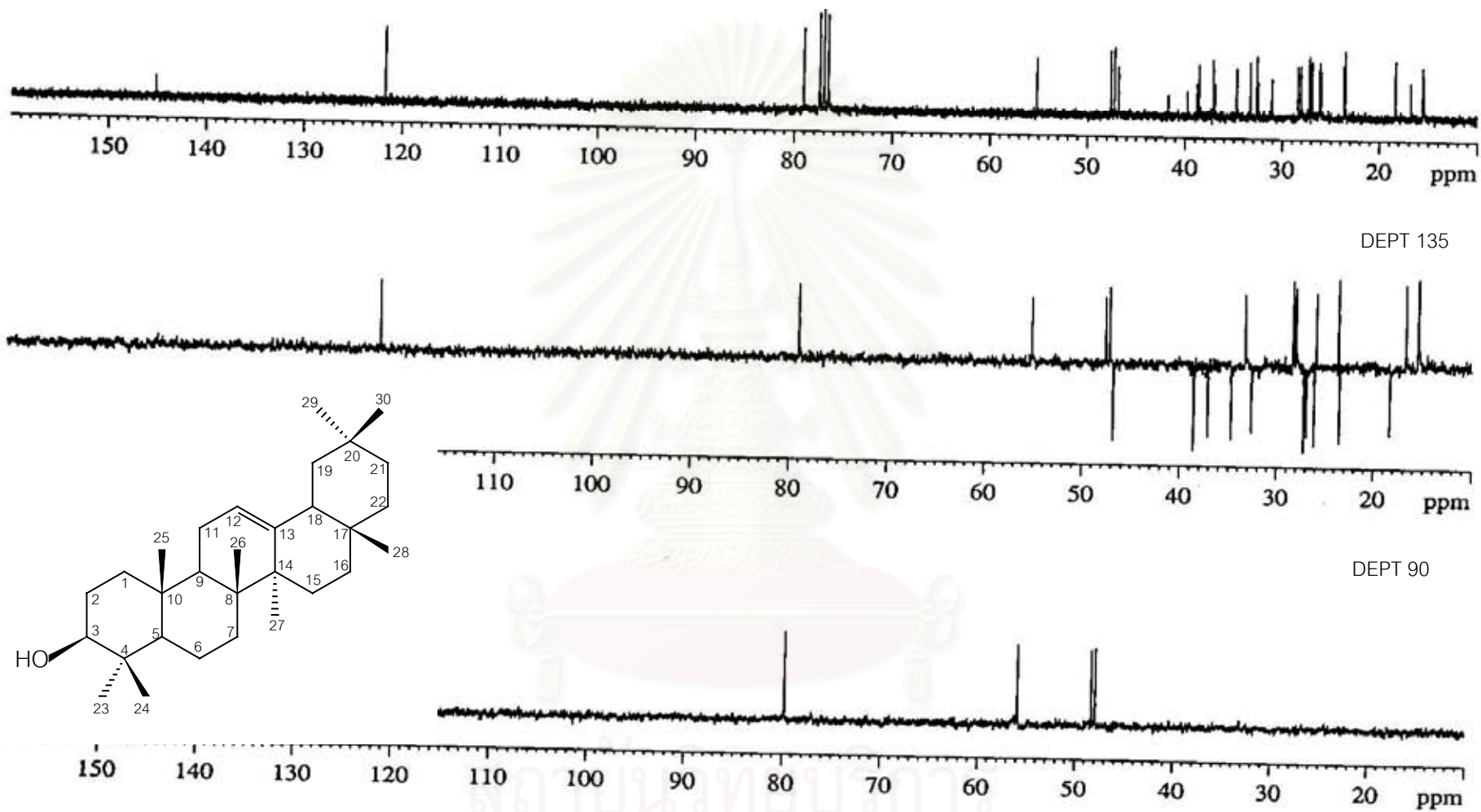


Figure 14a. The 75 MHz ^{13}C -DEPT NMR spectrum of compound DG2 (in CDCl_3)

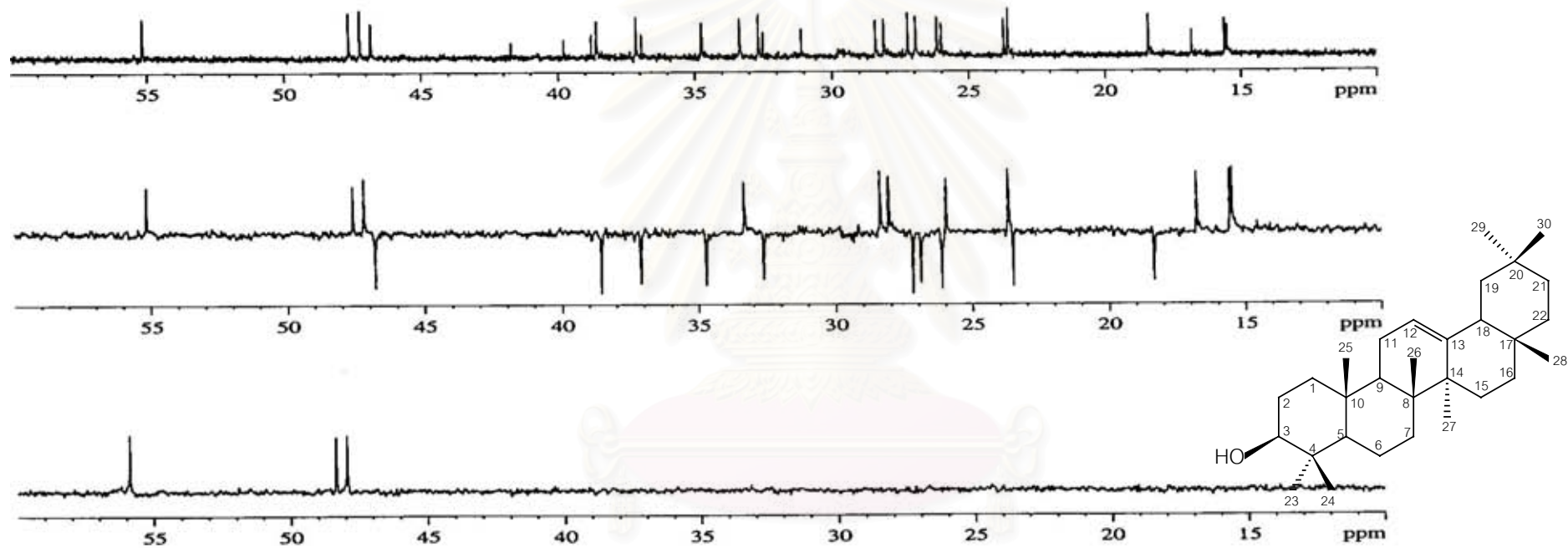


Figure 14b. The 75 MHz ^{13}C -DEPT NMR spectrum of compound DG2 (expanded)

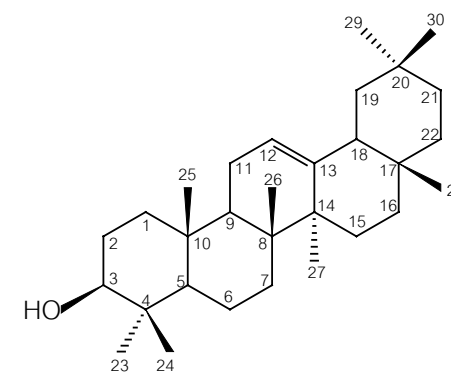
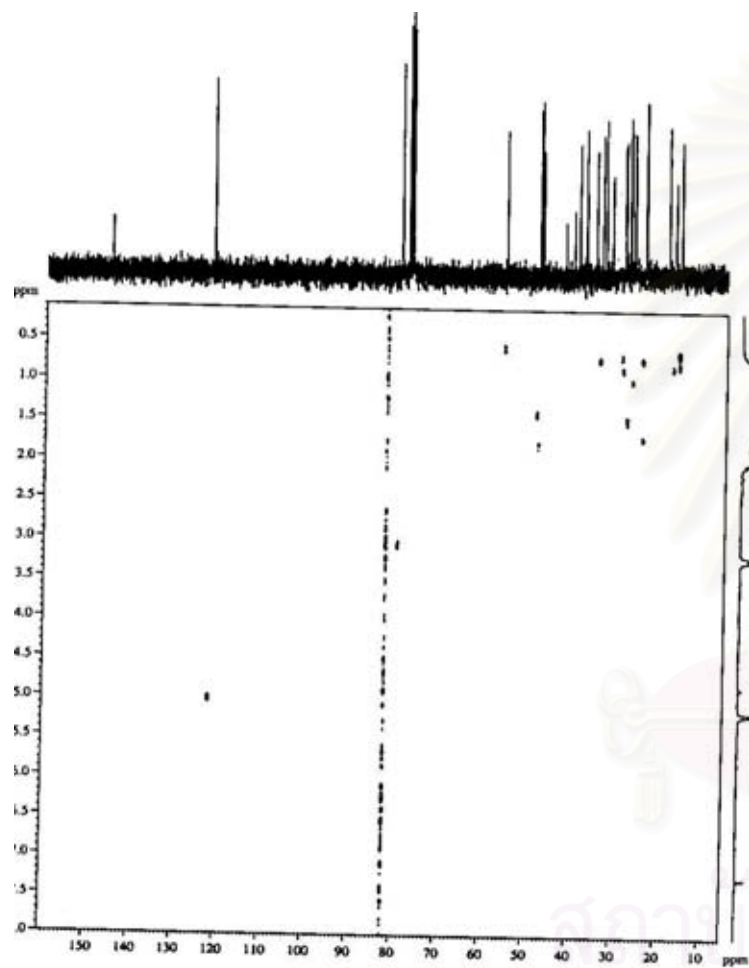


Figure 15a. The 75 MHz ^1H - ^{13}C HETCOR NMR spectrum of compound DG2 (in CDCl_3)

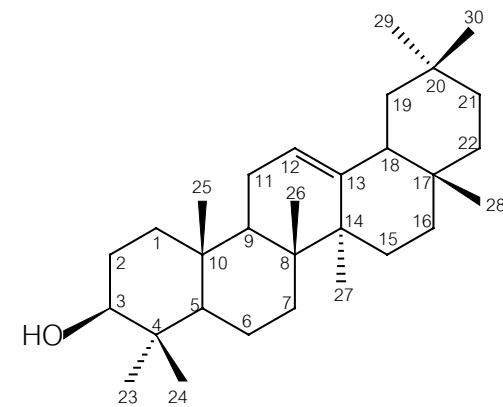
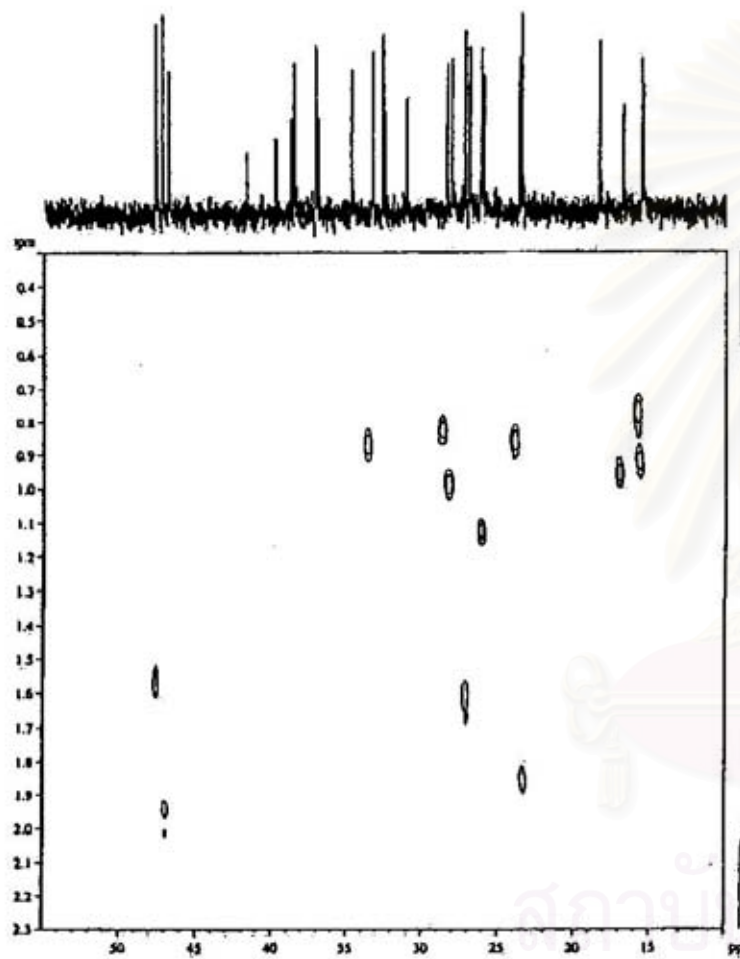


Figure 15b. The 75 MHz ^1H - ^{13}C HETCOR NMR spectrum of compound DG2 (expanded)

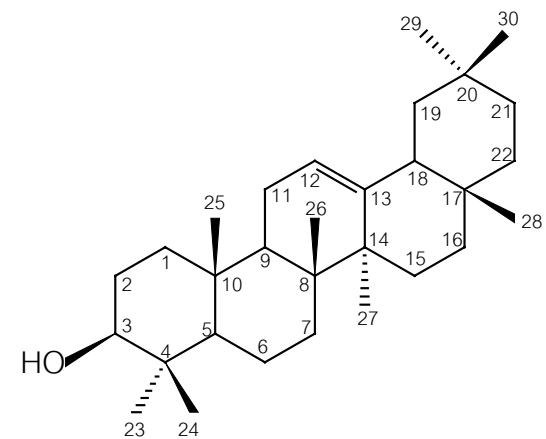
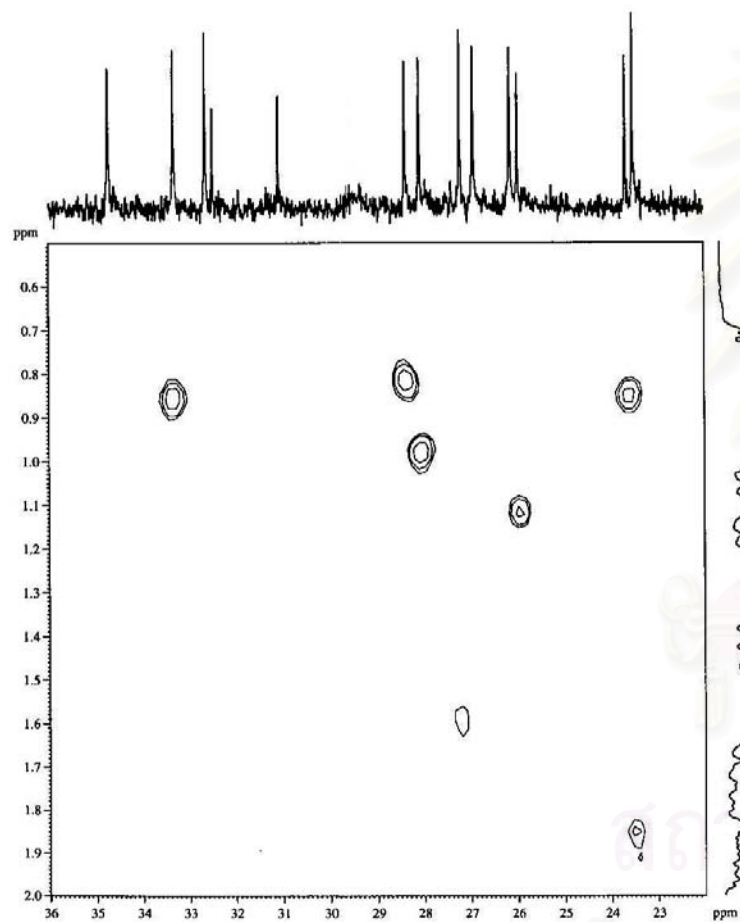


Figure 15c. The 75 MHz ^1H - ^{13}C HETCOR NMR spectrum of compound DG2 (expanded)

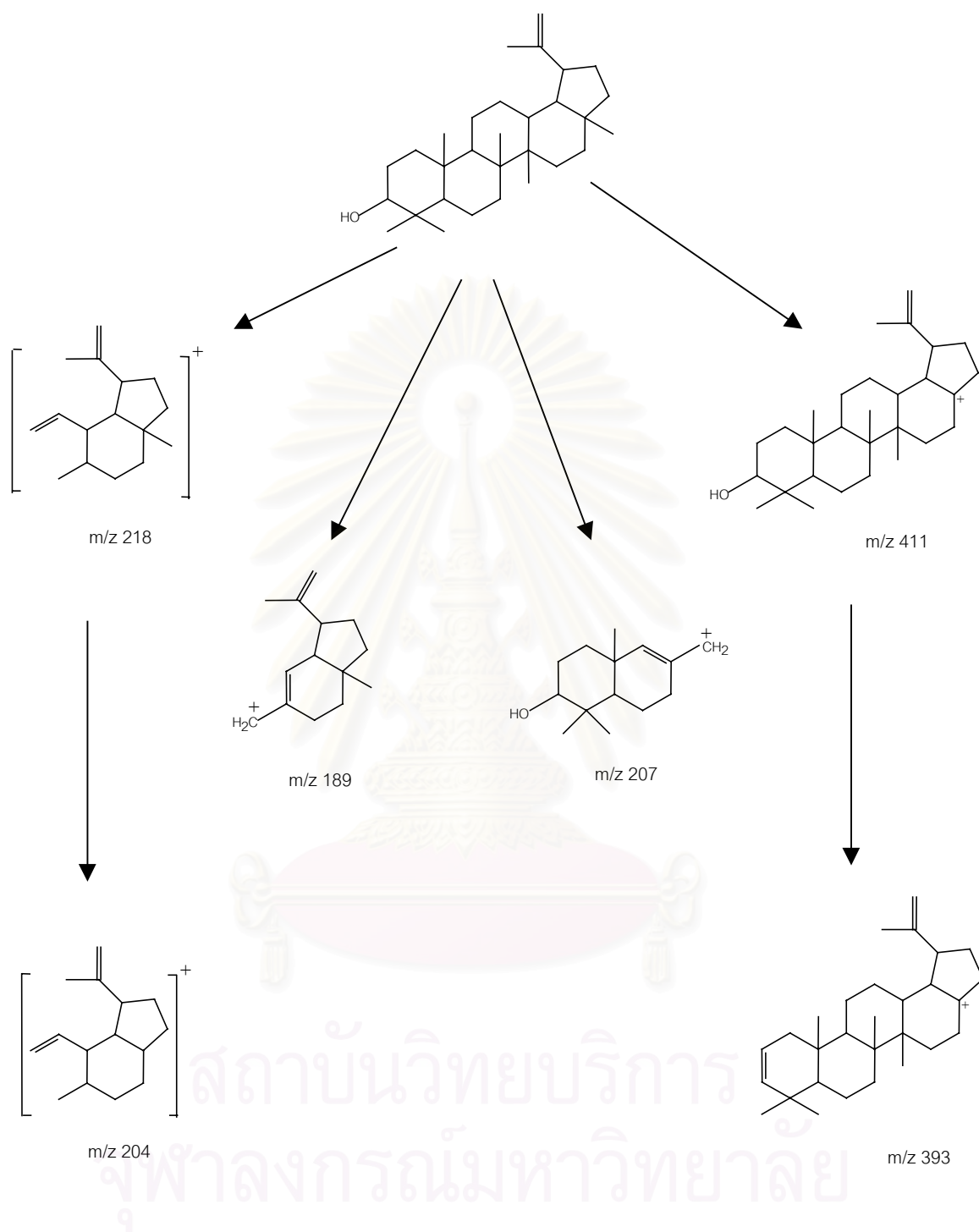
3. Identification of Compound DG3

Compound DG3 was recrystallized as white powder from methanol (58.5 mg, 0.01% yield). The compound gave purple color to Liebermann-Burchard reagent, suggesting that it is a triterpenoid. Its EIMS (Figure 16) showed a molecular ion peak at m/z 426 which corresponded to the molecular formula of $C_{30}H_{50}O$. The base peak at m/z 189 suggested that DG3 has a skeleton structure of the lupane type (Ogunkoya, 1981). The prominent peak at m/z 218 was the result of cleavage across the C ring of the lupane skeleton, and successive loss of a methyl group produced the fragment peak at m/z 204. The peaks at m/z 411 ($M-CH_3$) and m/z 393 ($M-CH_3-H_2O$) were also observed (Scheme 8). The IR spectrum (Figure 17) showed absorption band at 3486 cm^{-1} , indicating the presence of a hydroxyl substituent.

The $^1\text{H-NMR}$ spectrum (Figure 18) exhibited seven singlets of tertiary methyls at δ 0.74, 0.76, 0.81, 0.92, 0.94, 1.01, and 1.66 ppm). A double doublet (1H, $J = 5.1, 10.2$ Hz) at δ 3.17 ppm, assignable to the carbinylic proton (H-3), was typical for a triterpenoid with 3-OH substituent. A pair of broad singlets at δ 4.55 and 4.67 ppm could be assigned as exomethylene protons (H-29) in the isopropenyl group of a lupane-type triterpenoid.

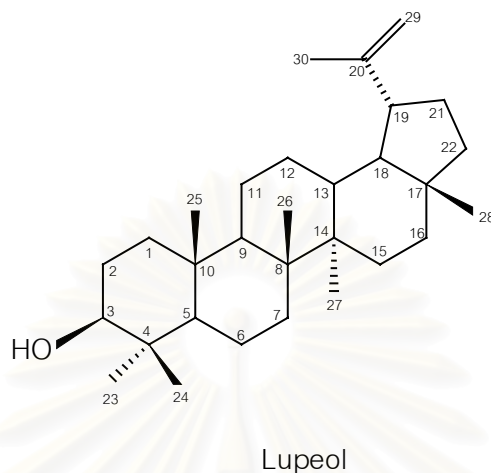
The $^{13}\text{C-NMR}$ spectrum of DG3 (Figure 19) showed 30 carbon signals, supportive of a triterpenoid structure. The DEPT and HETCOR experiments (Figures 20, 21) displayed signals for seven methyl carbons at δ 14.5, 15.4, 16.0, 16.1, 18.0, 19.3 and 28.0 ppm, eleven methylene carbons at δ 18.3, 20.9, 25.1, 27.4, 27.4, 29.9, 34.3, 35.6, 38.7, 40.0 and 109.3 ppm, six methine carbons at δ 38.0, 48.0, 48.3, 50.4, 55.3 and 79.0 ppm and six quaternary carbons at δ 37.2, 38.9, 40.8, 42.8, 43.0 and 151.0 ppm.

$^{13}\text{C-NMR}$ data of DG3 were found to be in full agreement with those previously reported for lupeol, (Reynolds *et. al*, 1986). Comparison of $^{13}\text{C-NMR}$ assignments of DG3, and lupeol together with $^1\text{H-NMR}$ assignment of DG3 are shown in Table 17.



Scheme 8. Mass fragmentation of compound DG3

DG3 was therefore identified as lupeol, the structure of which is shown below.



Lupeol was previously isolated from several species from ebenaceous plants, i.e. *Diospyros ebenum* (Gupta and Mahadevan, 1967), *D. rhodocalyx* (Musgrave and Skoyles, 1974) and *D. greeniwayi* (Khan and Rewekika, 1998). The compound has been reported as possessing antimycobacterial (Cantrell, Franzblau and Fischer, 2001), anti-inflammatory and analgesic activities (Ana, *et al.*, 2000). Lupeol from hexane extract of *D. maritima* showed potent cytotoxicity against Hepa-3B (hepatoma), Hela, (cervix carcinoma), Colo-205 (Colon carcinoma) and KB (nasopharynx carcinoma) cell, (Kou, *et al.*, 1997).

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Table 16. ^1H and ^{13}C -NMR assignments of compound DG3 (in CDCl_3) and the reported ^{13}C -NMR data of lupeol (in CDCl_3)

position	Compound DG3		Lupeol
	δ H (ppm)	δ C (ppm)	δ C (ppm)
1	-	38.7	38.7
2	-	27.4	27.4
3	3.17 (<i>dd</i> , $J=$ Hz)	79.0	78.9
4	-	38.9	38.8
5	0.66 (<i>d</i> , $J=8.7$ Hz)	55.3	55.3
6	-	18.3	18.3
7	-	34.3	34.2
8	-	40.8	40.8
9	-	50.4	50.4
10	-	37.2	37.1
11	-	20.9	20.9
12	-	25.1	25.1
13	-	38.0	38.0
14	-	42.8	42.8
15	-	27.4	27.4
16	-	35.6	35.5
17	-	43.0	43.0
18	-	48.3	48.2
19	2.36 (<i>m</i>)	48.0	47.9
20	-	151.0	150.9
21	-	30.0	29.8
22	-	40.0	40.0
23	0.94 (<i>s</i>)	28.0	28.0
24	0.74 (<i>s</i>)	15.4	15.4
25	0.81 (<i>s</i>)	16.1	16.1
26	1.01 (<i>s</i>)	16.0	15.9
27	0.92 (<i>s</i>)	14.5	14.5
28	0.76 (<i>s</i>)	18.0	18.0
29	4.55 (<i>br. s</i>), 4.67 (<i>br. s</i>)	109.3	109.3
30	1.66 (<i>s</i>)	19.3	19.3

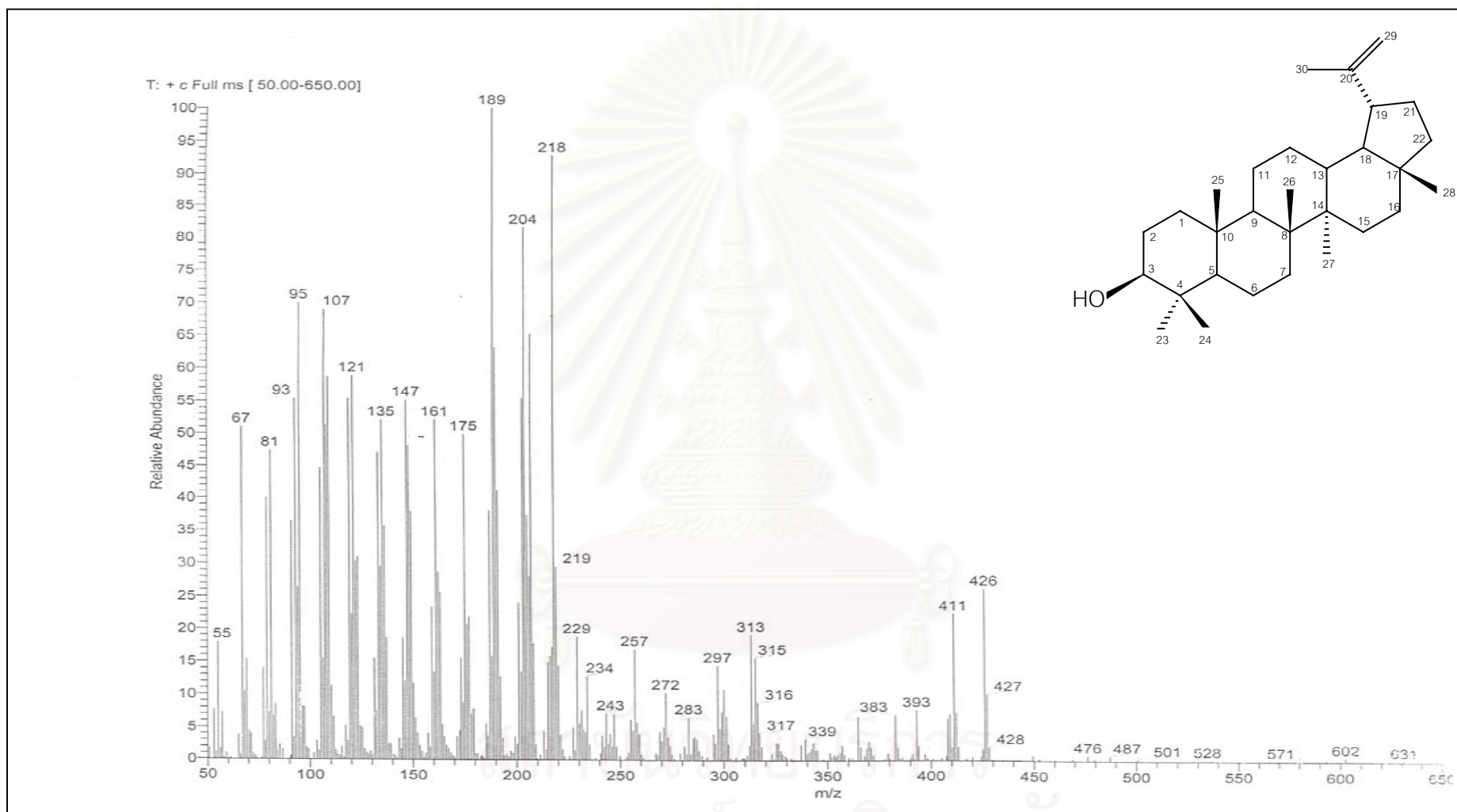


Figure 16. EIMS of compound DG3

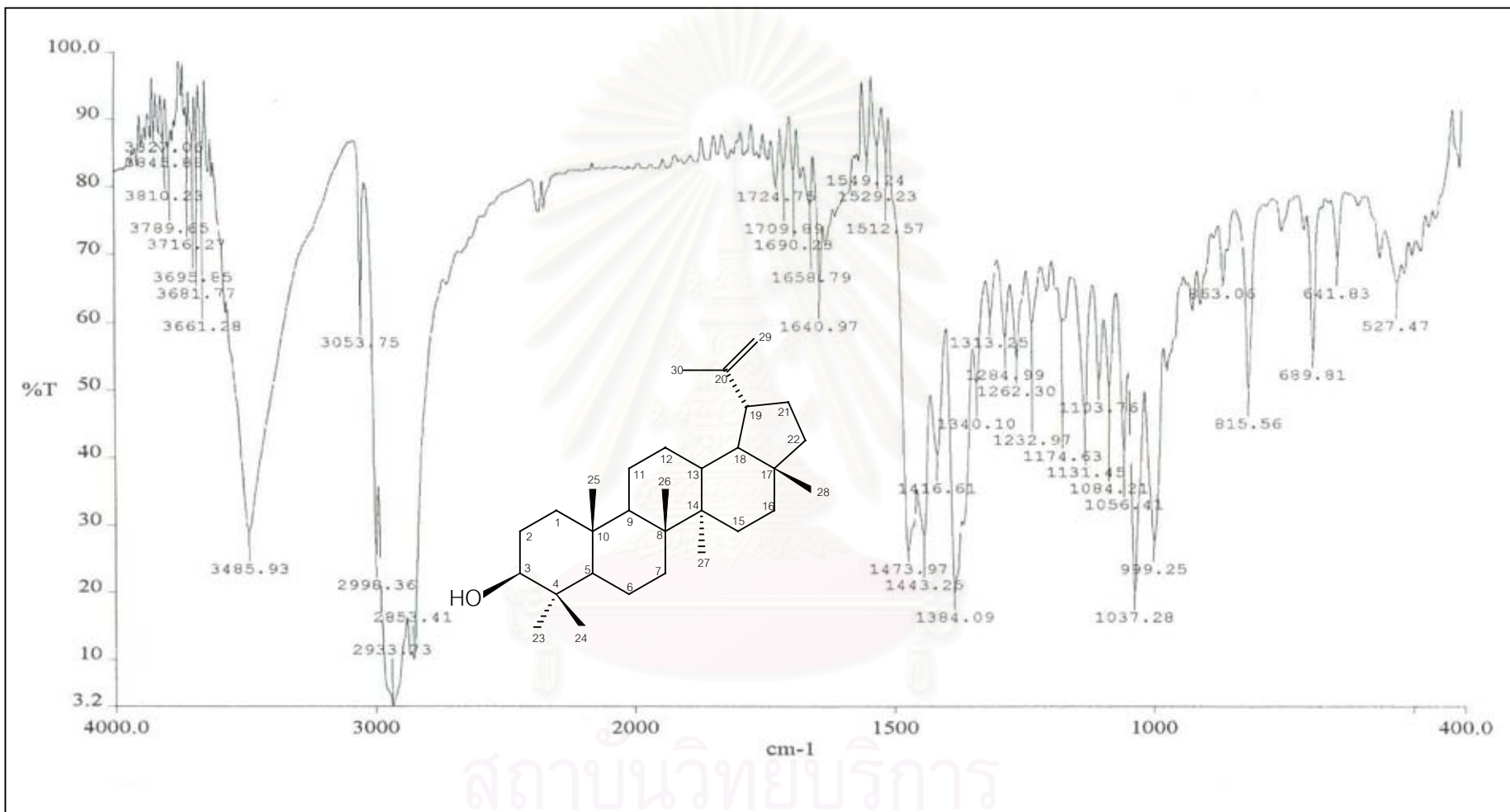


Figure 17. IR spectrum of compound DG3

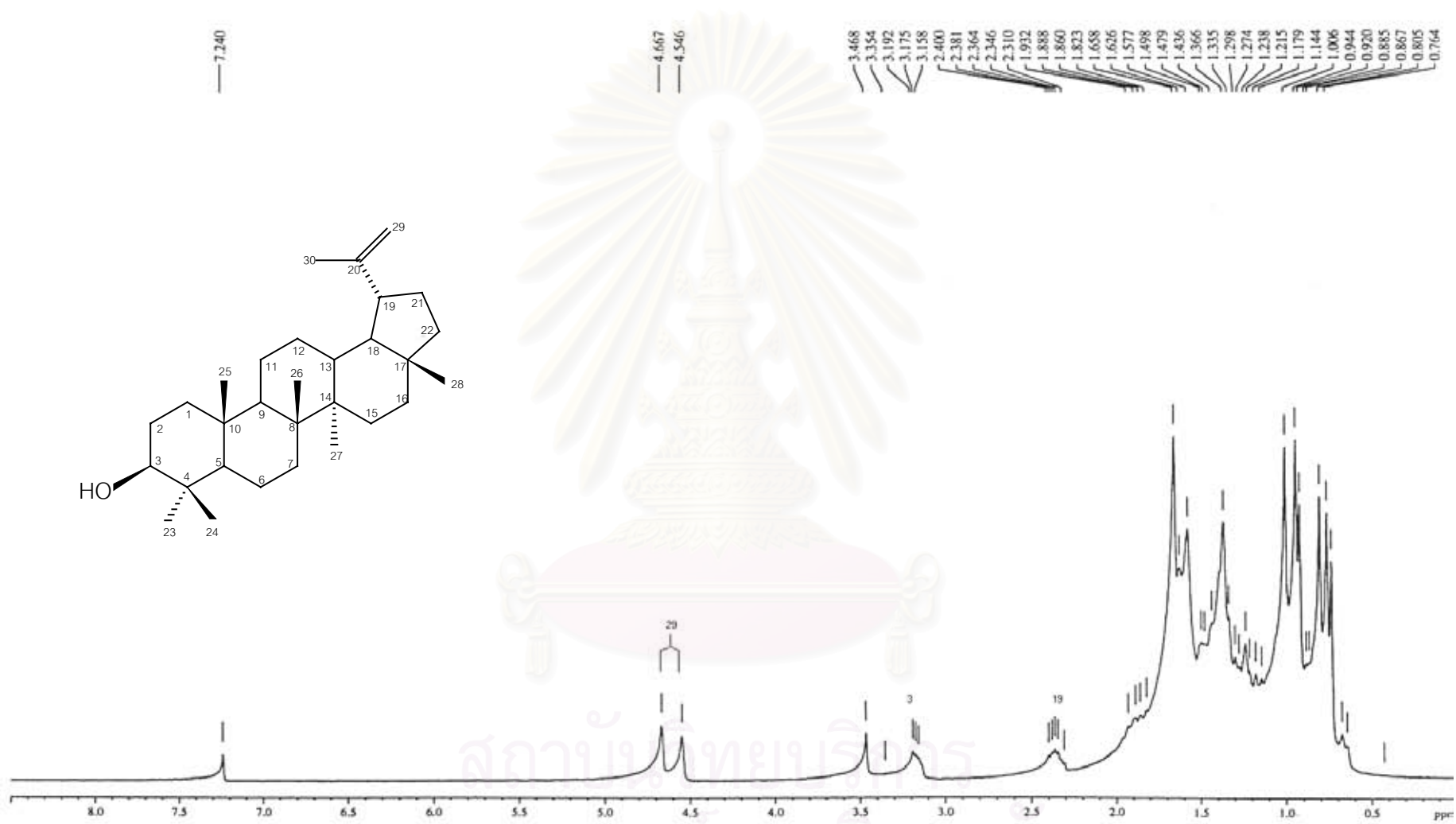


Figure 18a. The 300 MHz ^1H NMR spectrum of compound DG3 (in CDCl_3)

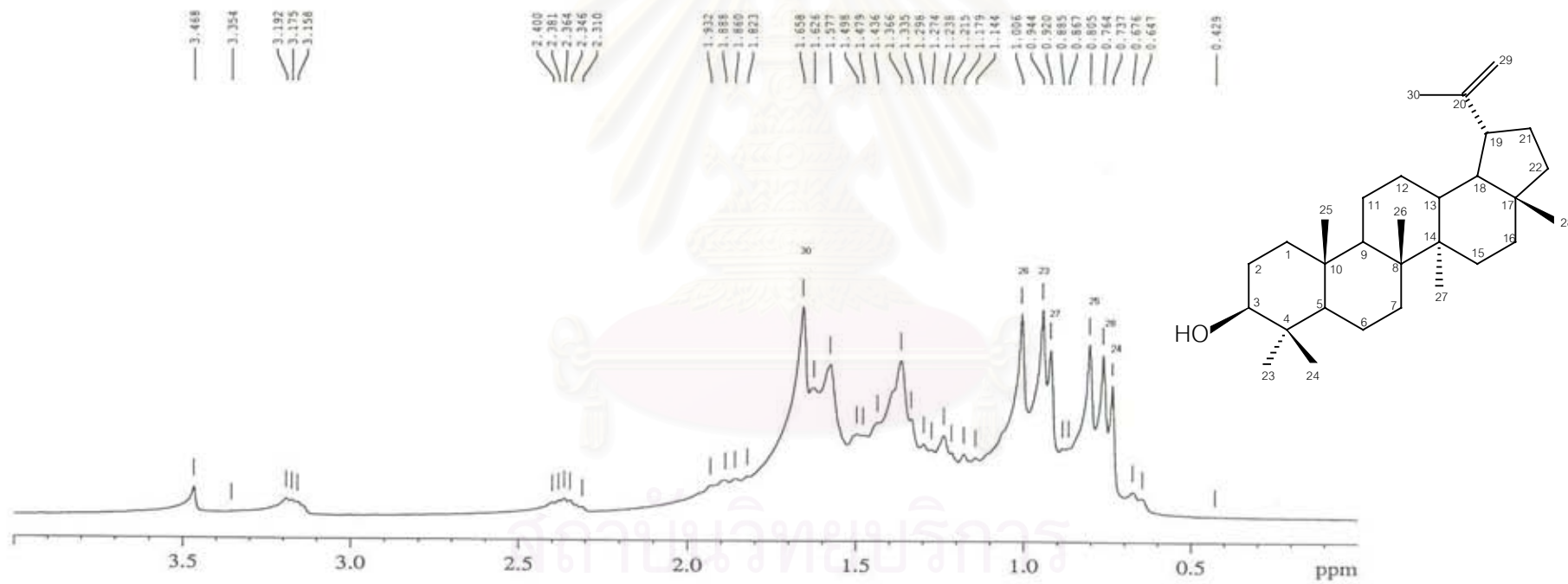


Figure 18b. The 300 MHz ¹H NMR spectrum of compound DG3 (expanded)

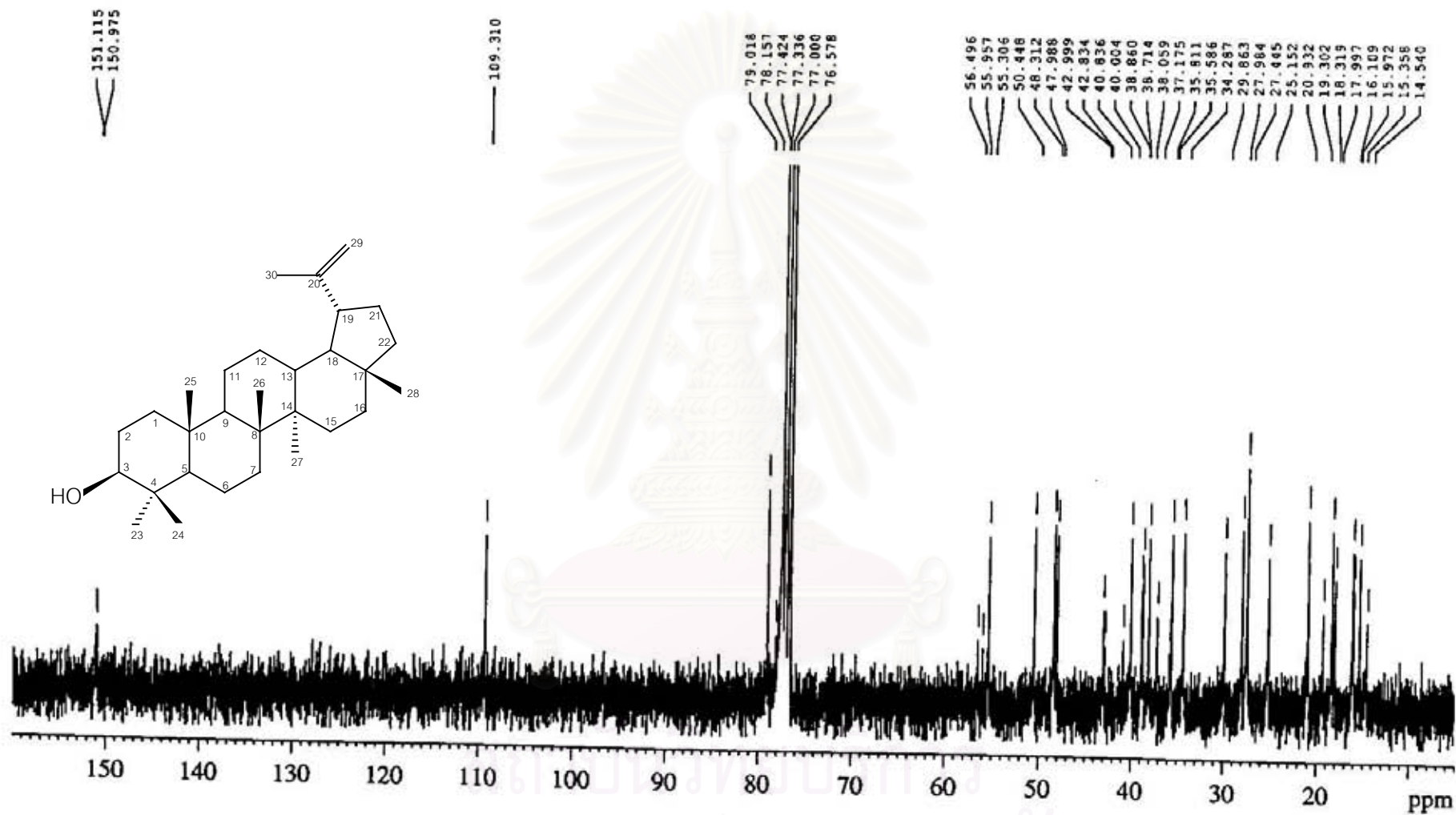


Figure 19a. The 75 MHz ¹³C NMR spectrum of compound DG3 (in CDCl₃)

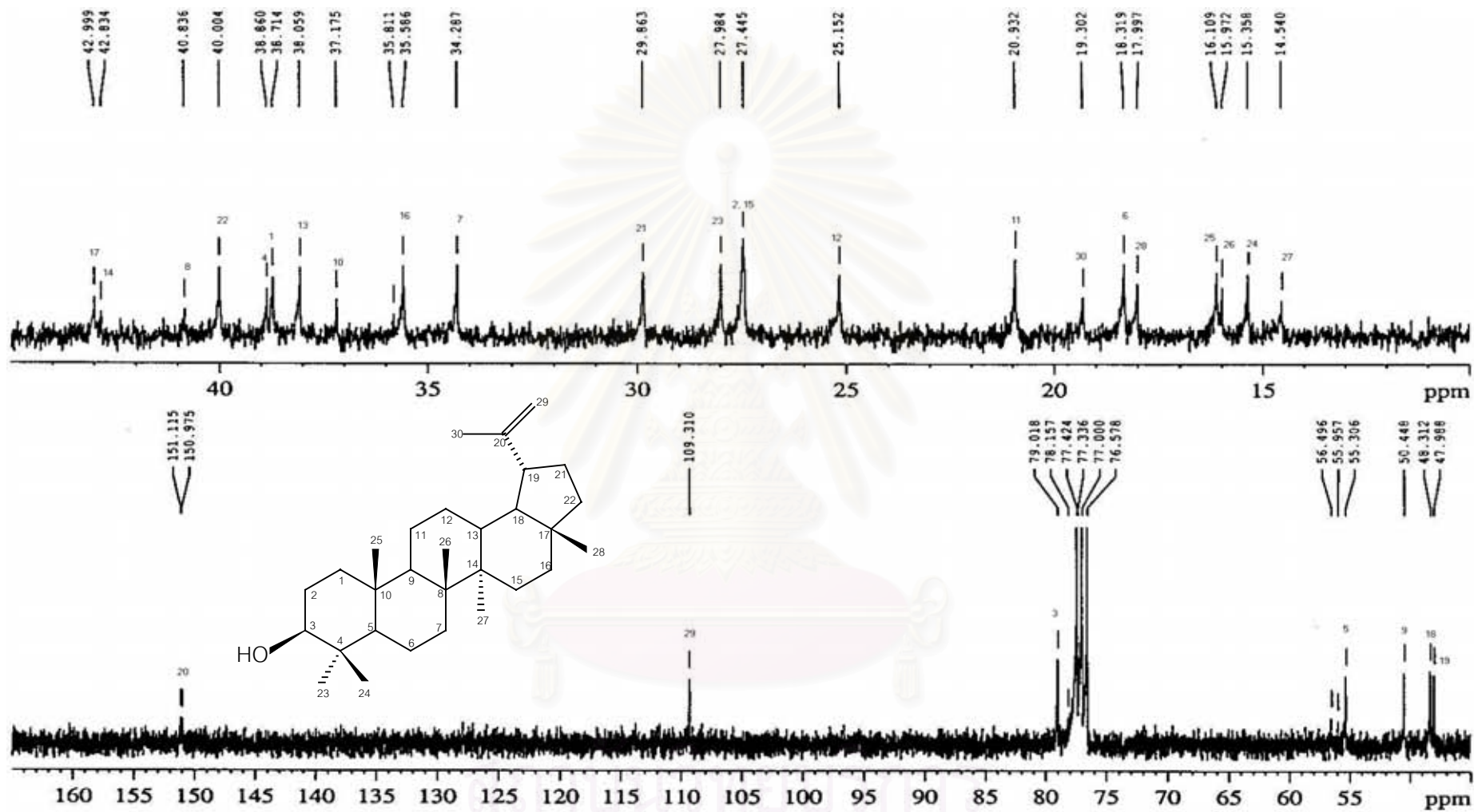


Figure 19b. The 75 MHz ^{13}C NMR spectrum of compound DG3 (expanded)

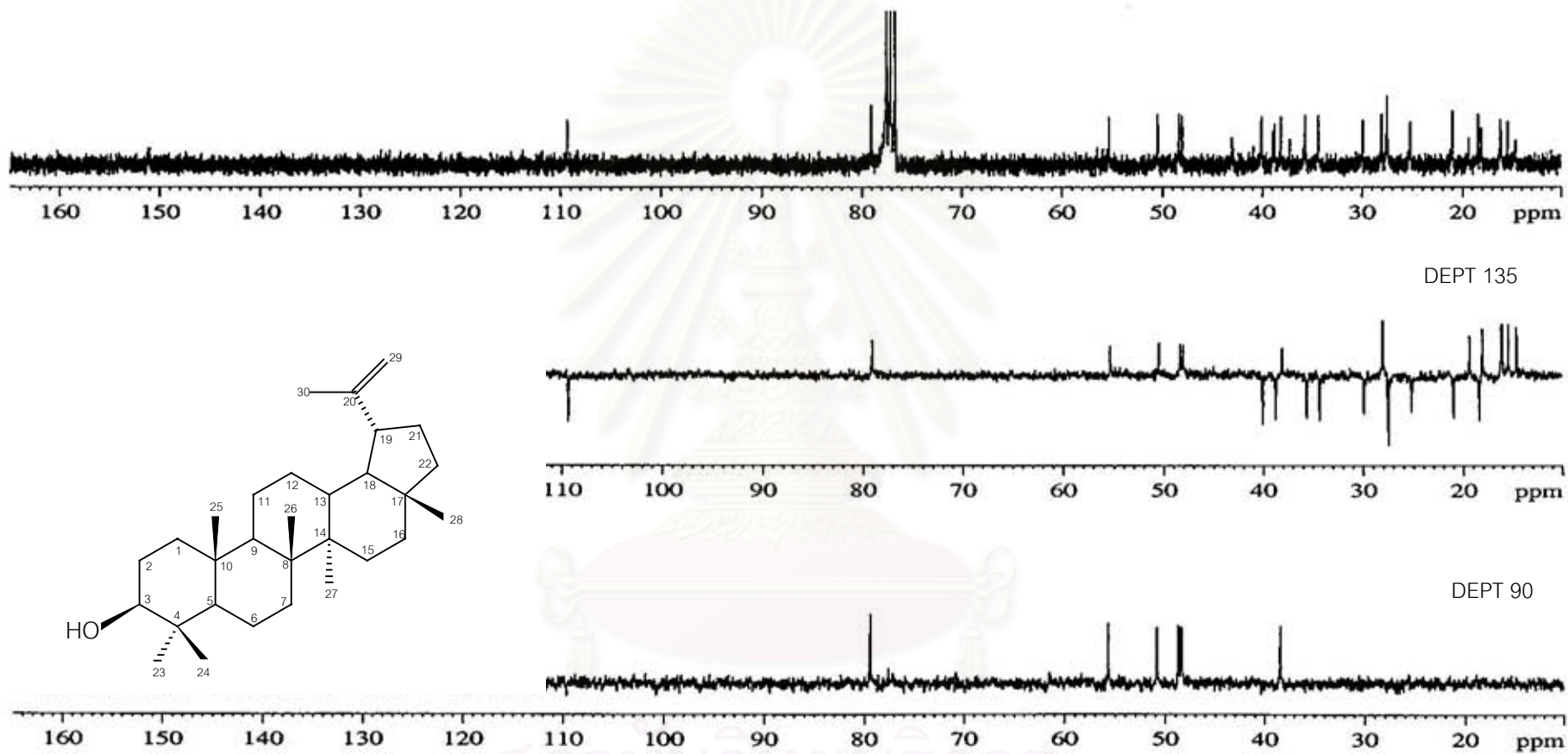


Figure 20a. The 75 MHz ^{13}C -DEPT NMR spectrum of compound DG3 (in CDCl_3)

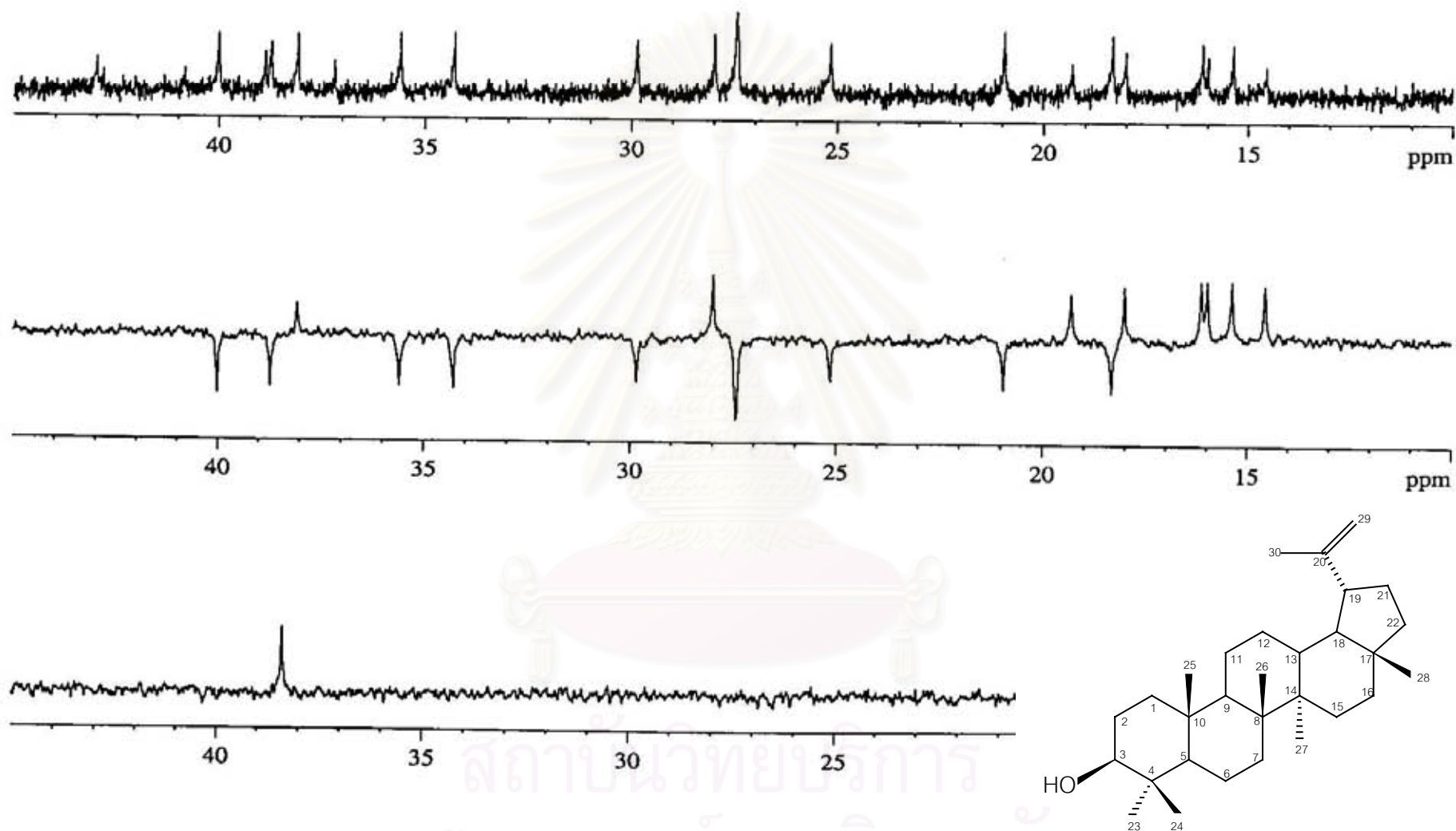


Figure 20b. The 75 MHz ^{13}C -DEPT NMR spectrum of compound DG3 (expanded)

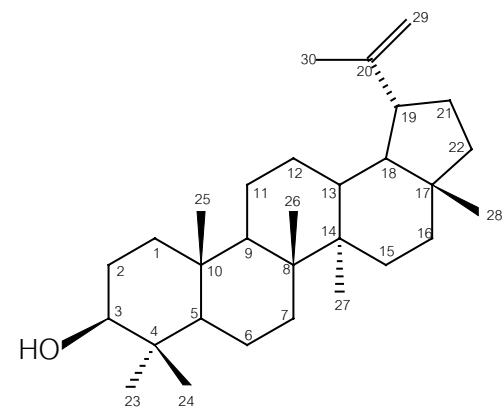
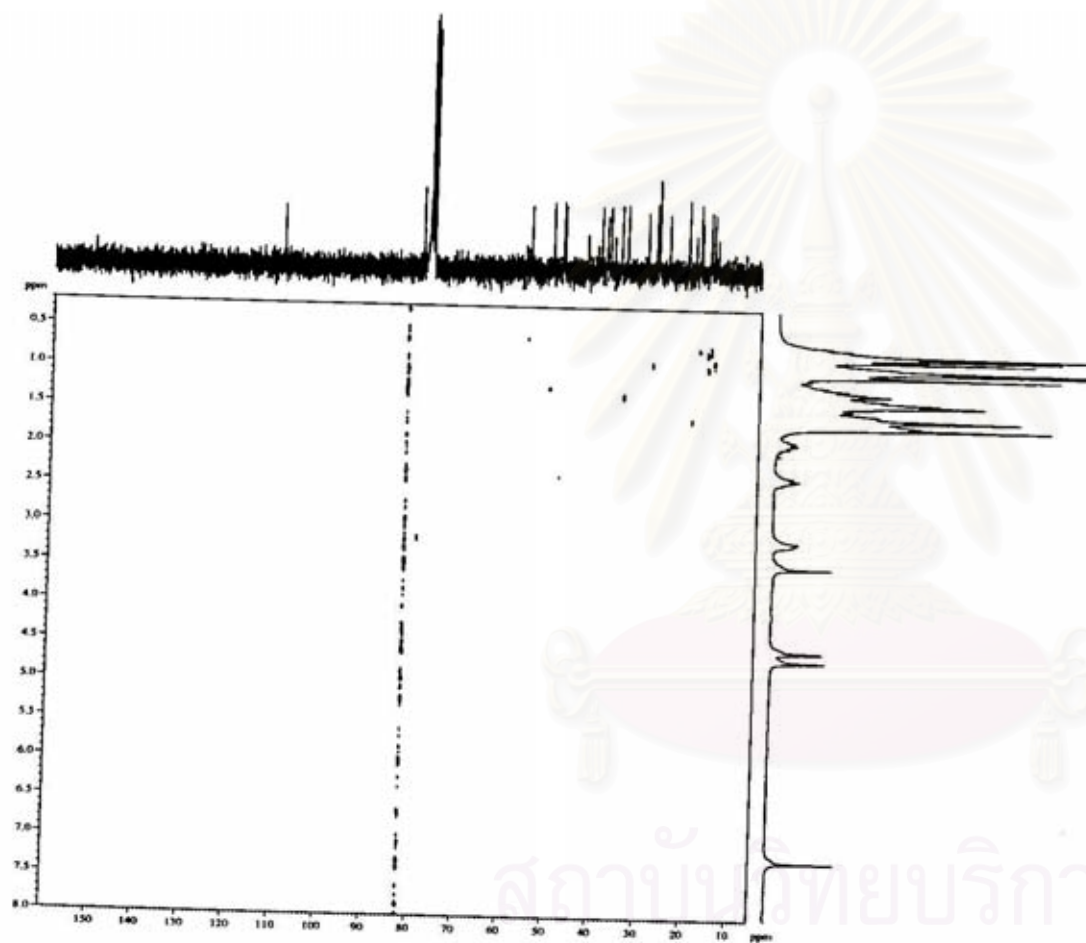


Figure 21. The 75 MHz ^1H - ^{13}C HETCOR NMR spectrum of compound DG3 (in CDCl_3)

4. Identification of Compound DG4

Compound DG4 was recrystallized as white amorphous powder from methanol (41.1 mg, 0.01% yield). This compound gave purple color to Liebermann-Burchard reagent, suggesting that it is a triterpenoid. Its EIMS (Figure 22) showed a molecular ion peak at m/z 442 which corresponded to the molecular formula of $C_{30}H_{50}O_2$. The intense fragment peak at m/z 189 was important in showing that DG4 has a skeleton structure of the lupane type (Ogunkoya, 1981). The IR spectrum (Figure 23) showed OH band at 3443 cm^{-1} .

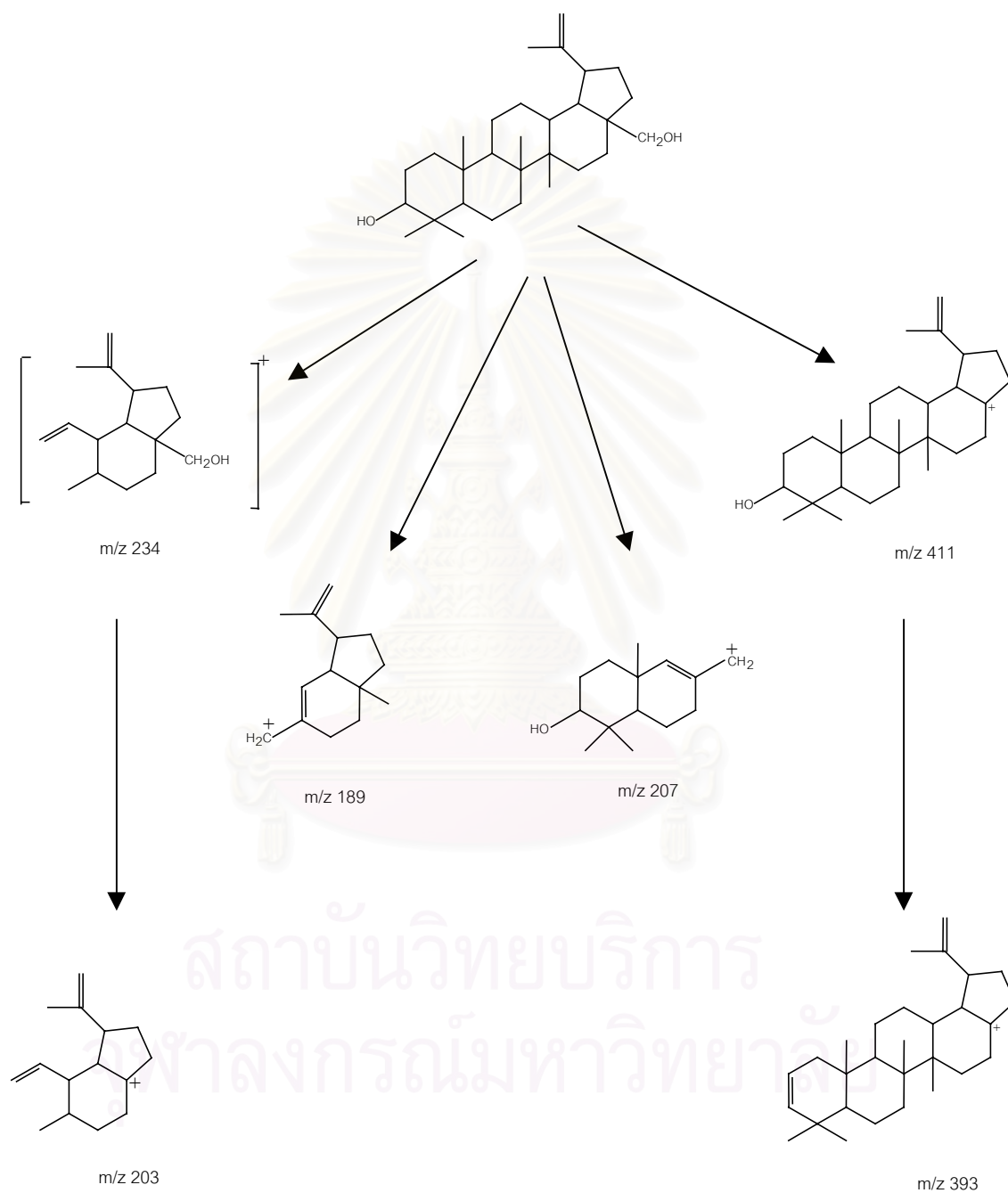
The $^1\text{H-NMR}$ spectrum of DG4 (Figure 24) was similar to that of DG3 except for the absence of one methyl singlet and the addition of a pair of doublets ($J= 10.8\text{ Hz}$) at δ 3.31 and 3.78 ppm. This information suggested a structure of lupeol derivative in which one methyl is replaced by the primary alcoholic group. A double doublet (1H, $J= 5.1, 10.8\text{ Hz}$) at δ 3.16 ppm and a pair of broad singlets at δ 4.56 and 4.66 ppm could be assigned to the carbonylic proton (H-3) and the exomethylene protons (H-29), respectively.

The $^{13}\text{C-NMR}$ spectrum of compound DG4 (Figure 25) showed 30 carbon signals. The DEPT and HETCOR experiments (Figures 26, 27) were employed to classify these signals into those of six methyl carbons at δ 14.7, 15.3, 16.0, 16.1, 19.1 and 28.0 ppm, twelve methylene carbons at δ 18.3, 20.8, 25.2, 27.0, 27.3, 29.2, 29.7, 33.9, 34.2, 38.7, 60.5 and 109.7 ppm, six methine carbons at δ 37.3, 47.8, 48.7, 50.4, 52.3 and 79.0 ppm, and the six quaternary carbons at δ 37.1, 38.8, 40.9, 42.7, 47.8 and 150.5 ppm.

Comparison of $^{13}\text{C-NMR}$ data of DG4 with those values previously reported for betulin (Tinto, *et al.*, 1992) suggested that they are the same compound. The ^1H and $^{13}\text{C-NMR}$ assignments of DG4 and the reported $^{13}\text{C-NMR}$ data of betulin are shown in Table 18.

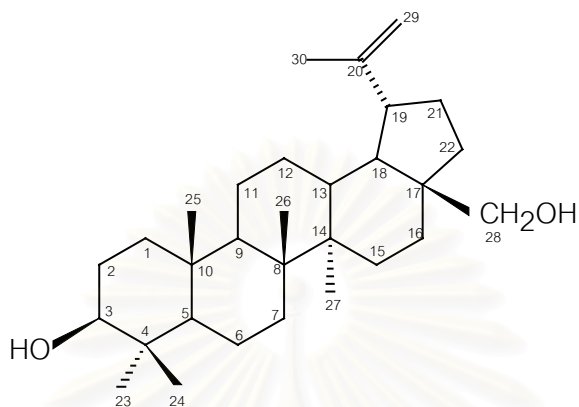
The EIMS also confirmed the structure of betulin. The mass fragment peaks at m/z 411 (M- CH_2OH) and 393 (M- $\text{CH}_2\text{OH-H}_2\text{O}$) could be observed. The peaks at m/z 207 and 234 were the results of cleavage at different positions across the C ring of lupane

skeleton. Successive loss of primary alcoholic group from the fragment ion at m/z 234 produced the mass fragment peak at m/z 203 ($234-31$). Mass fragmentation of DG4 is shown in Scheme 9.



Scheme 9. Mass fragmentation of compound DG4

Therefore, it was concluded that DG4 is betulin, the structure of which is shown below.



Betulin

Betulin was previously isolated from several species of ebenaceous plants, i.e. *Diospyros ismailii* (Zakaria, *et al.*, 1984), *D. leucomelas* (Recio, *et al.*, 1995), *D. virainiana* (Hayek, *et al.*, 1989). This compound has been reported as possessing antimycobacterial (Cantrell, *et al.*, 2001) and anti-inflammatory (Recio, *et al.*, 1995) activities.

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Table 18. ^1H and ^{13}C -NMR assignments of compound DG4 (in CDCl_3) and the reported ^{13}C -NMR data of Betulin (in CDCl_3)

position	Compound DG4		Betulin
	δ H (ppm)	δ C (ppm)	δ C (ppm)
1	-	38.7	38.8
2	-	27.0	27.2
3	3.16 (<i>dd</i> , $J = 10.8$ Hz)	79.0	78.9
4	-	38.8	38.9
5	0.66 (<i>d</i> , $J = 9.3$ Hz)	55.3	55.3
6	-	18.3	18.3
7	-	34.2	34.3
8	-	40.9	40.9
9	-	50.4	50.4
10	-	37.1	37.2
11	-	20.8	20.9
12	-	25.2	25.3
13	-	37.3	37.3
14	-	42.7	42.7
15	-	27.3	27.0
16	-	29.2	29.2
17	-	47.8	47.8
18	-	48.7	48.8
19	2.36 (<i>m</i>)	47.8	47.8
20	-	150.5	150.6
21	-	29.7	29.8
22	-	33.9	34.0
23	0.95(<i>s</i>)	28.0	28.0
24	0.74(<i>s</i>)	15.3	15.4
25	0.80(<i>s</i>)	16.1	16.1
26	1.00(<i>s</i>)	16.0	16.0
27	0.96(<i>s</i>)	14.7	14.8
28	3.31 (<i>d</i> , $J = 10.8$ Hz), 3.78 (<i>d</i> , $J = 10.8$ Hz)	60.5	60.2
29	4.56 (<i>br. s</i>), 4.66 (<i>br. s</i>)	109.7	109.6
30	1.66(<i>s</i>)	19.1	19.1

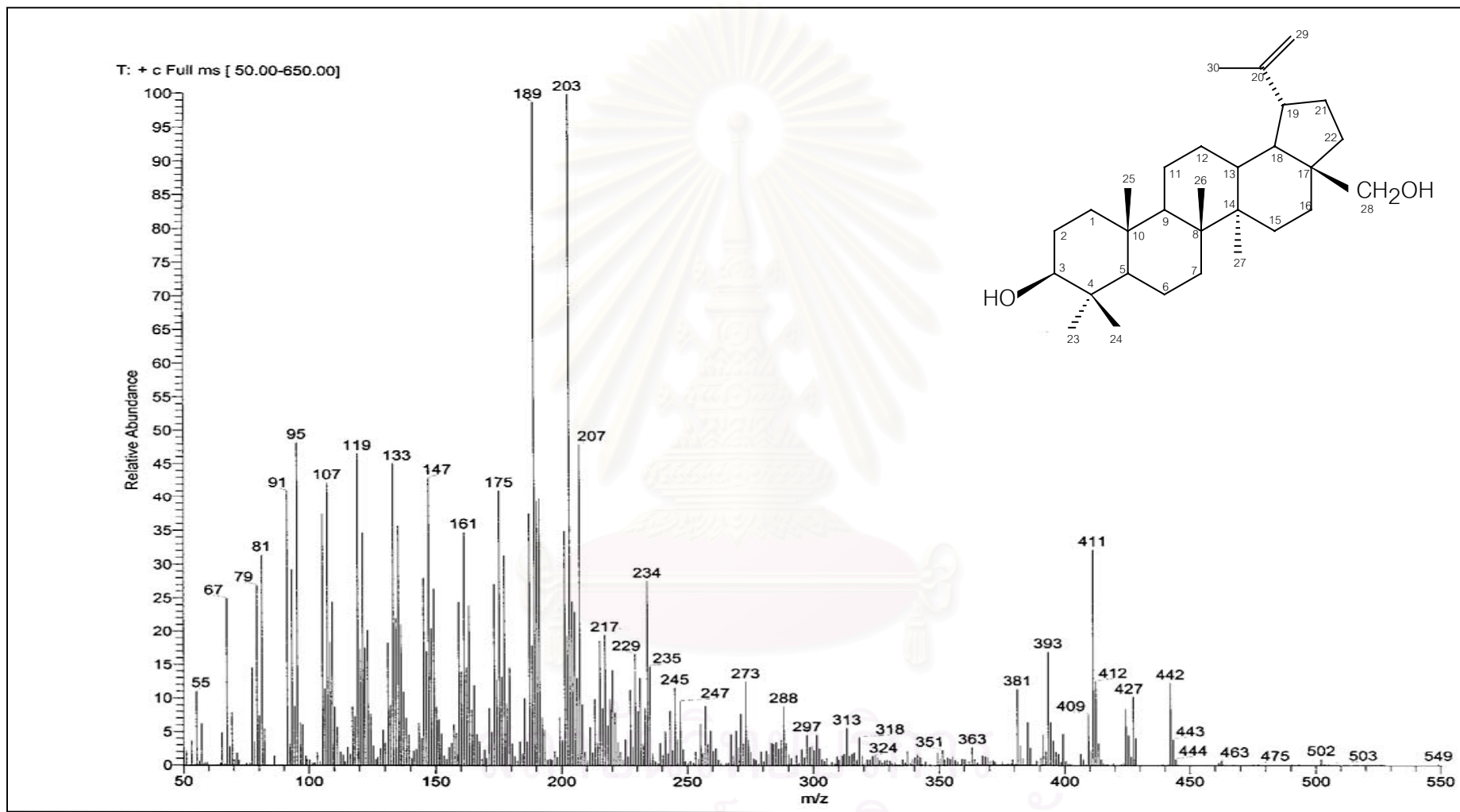


Figure 22. EIMS of compound DG4

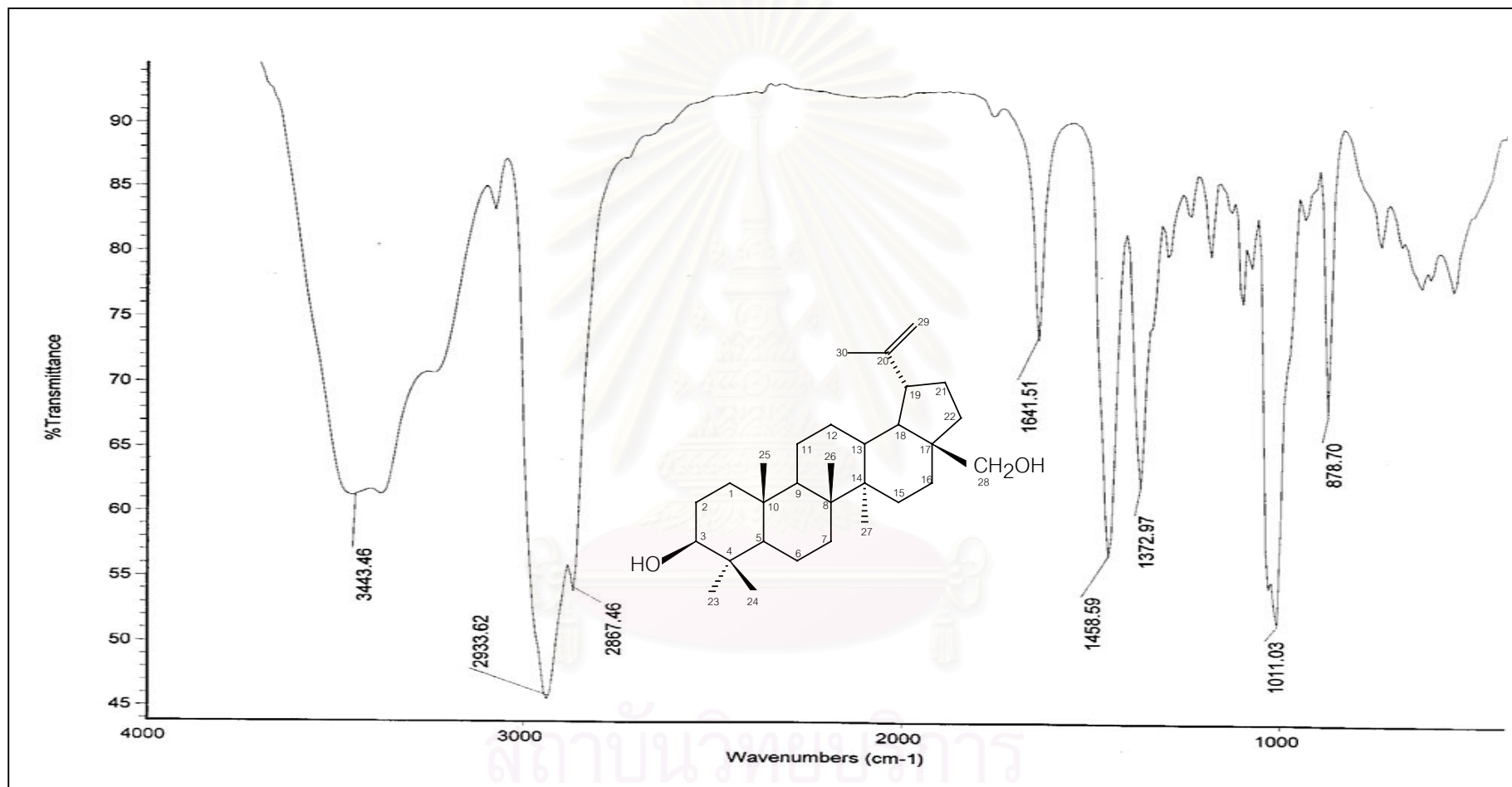


Figure 23. IR spectrum of compound DG4

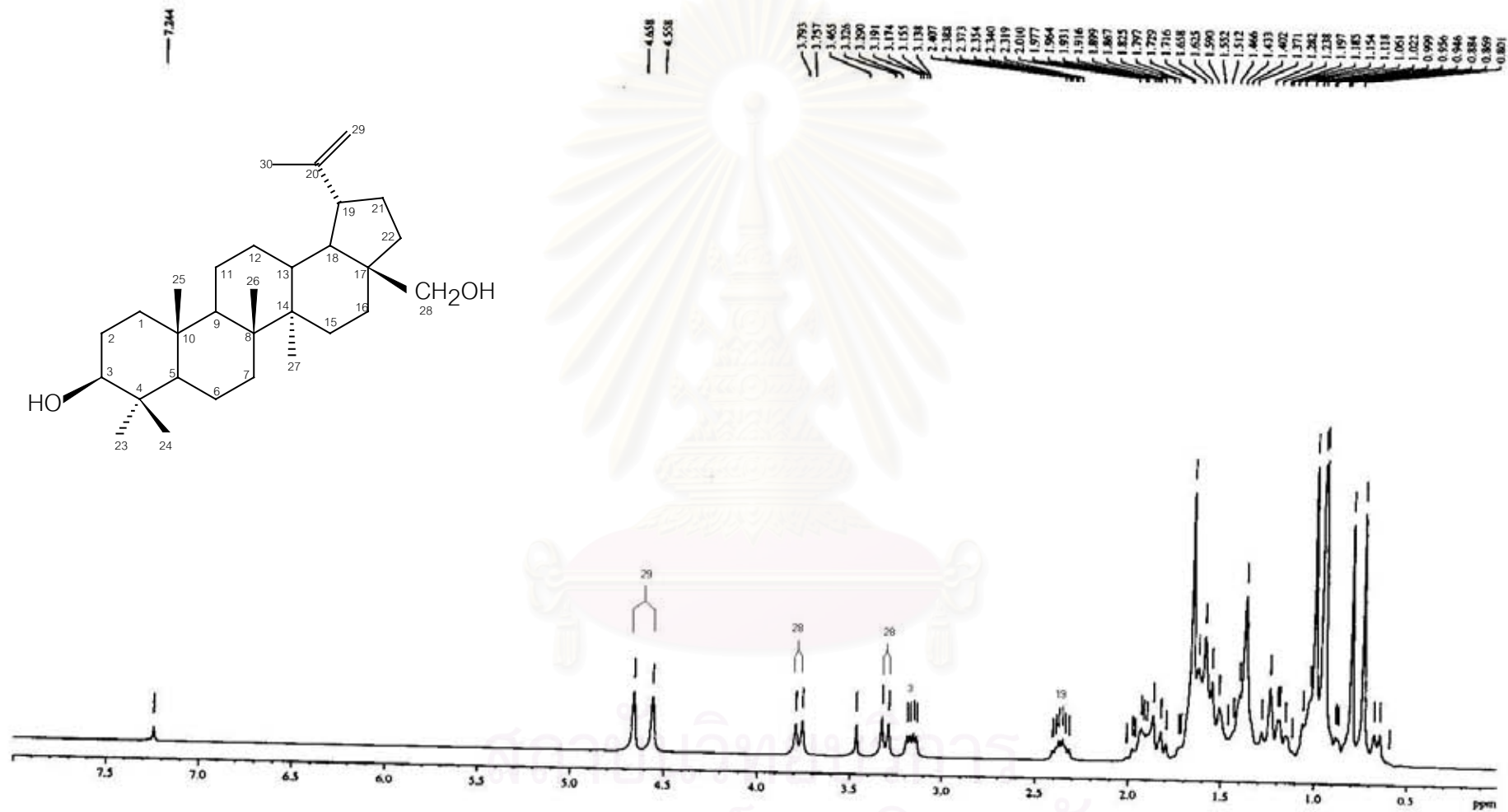


Figure 24a. The 300 MHz ¹H-NMR spectrum of compound DG4 (in CDCl₃)

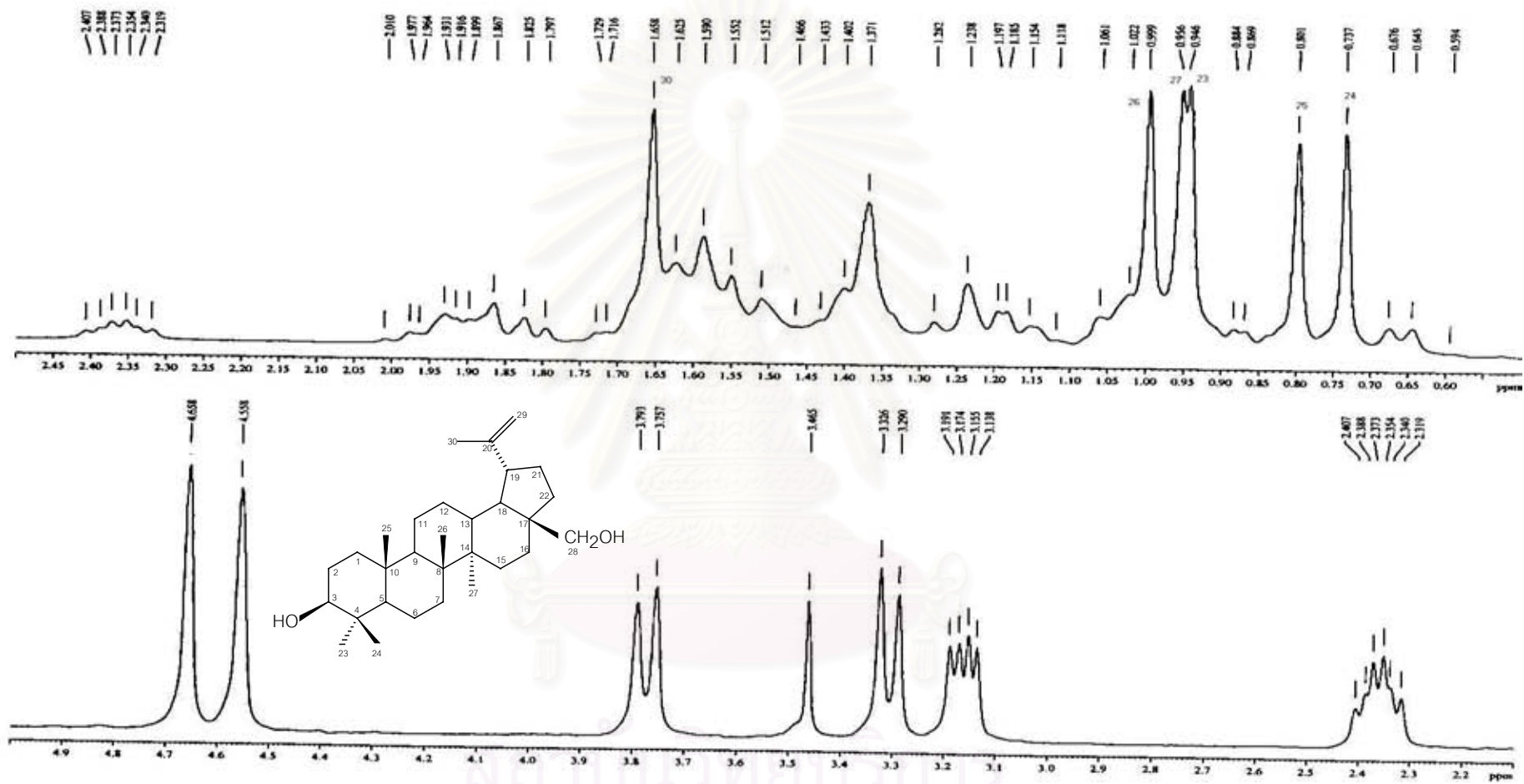


Figure 24b. The 300 MHz ¹H-NMR spectrum of compound DG4 (expanded)

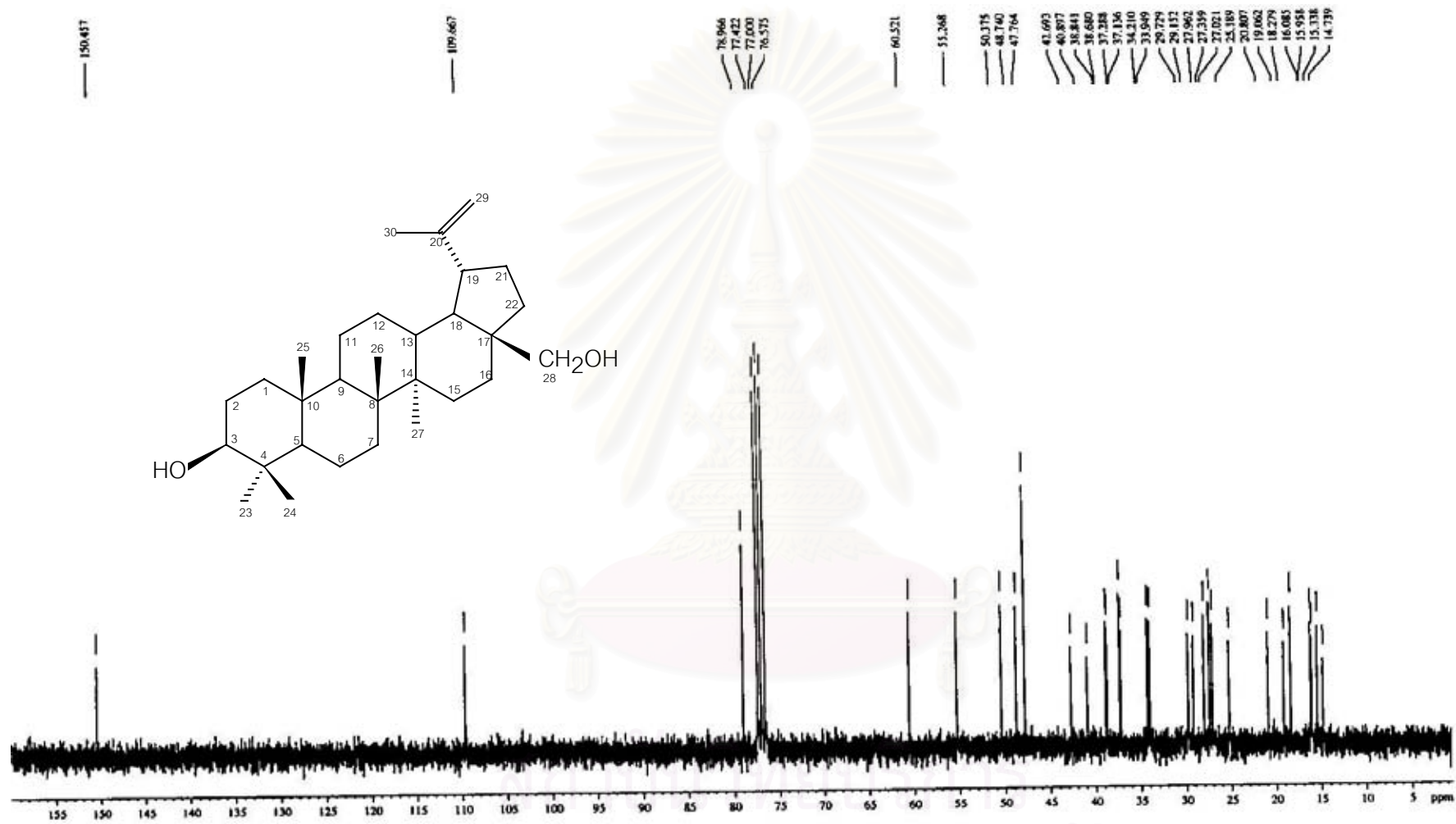


Figure 25a. The 75 MHz ¹³C-NMR spectrum of compound DG4 (in CDCl₃)

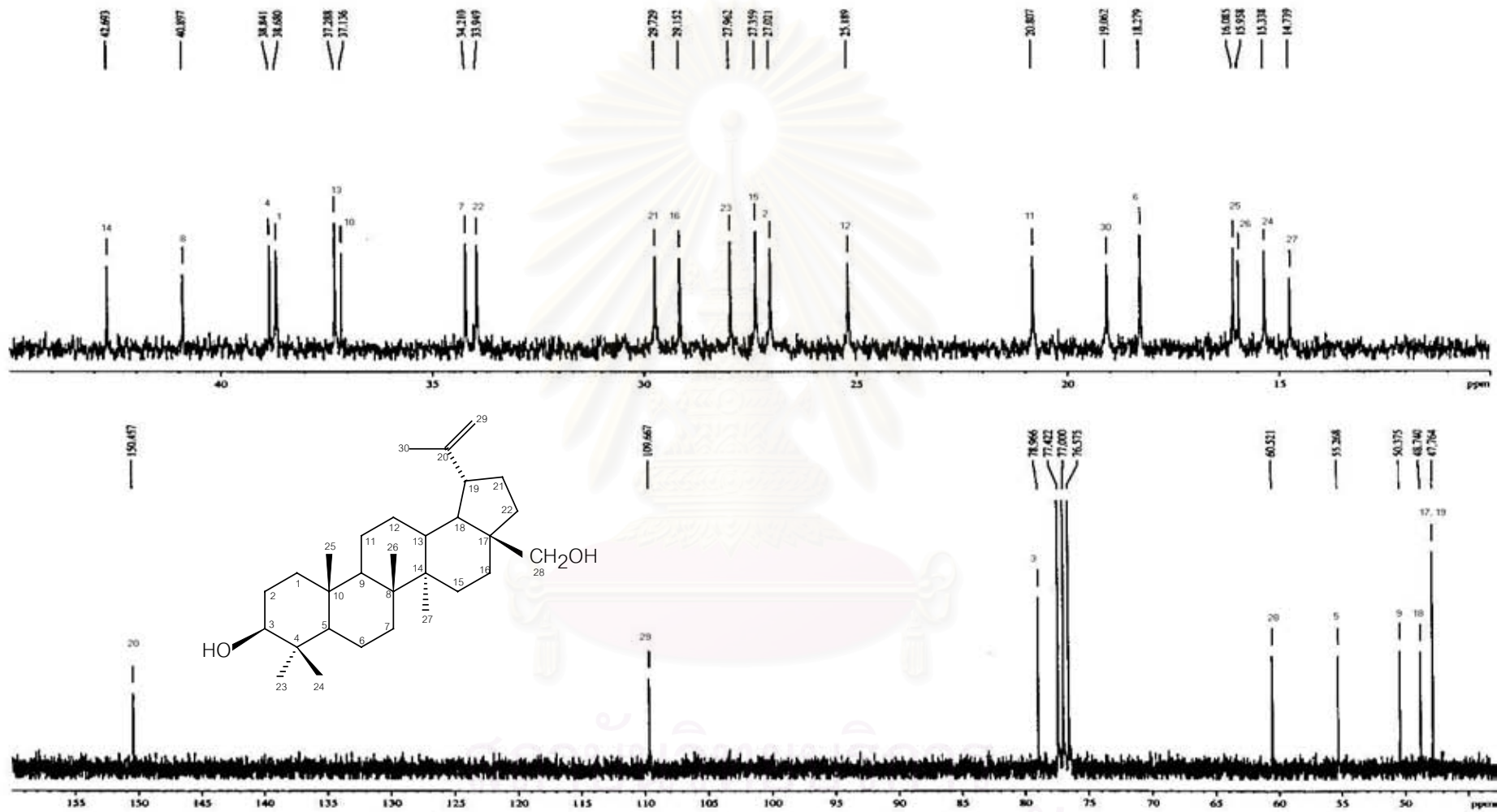


Figure 25b. The 75 MHz ¹³C-NMR spectrum of compound DG4 (expanded)

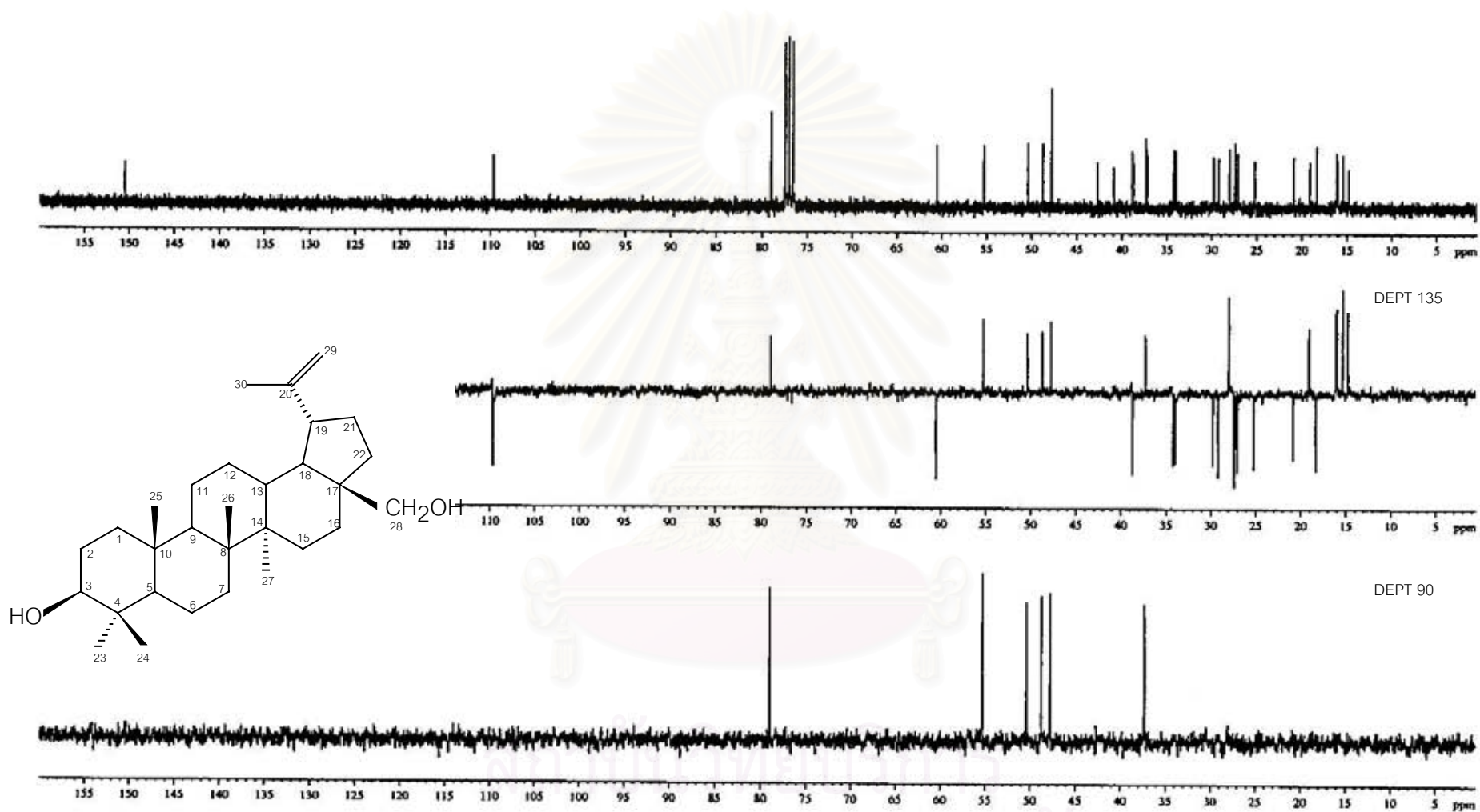


Figure 26. The 75 MHz ^{13}C -DEPT NMR spectrum of compound DG4 (in CDCl_3)

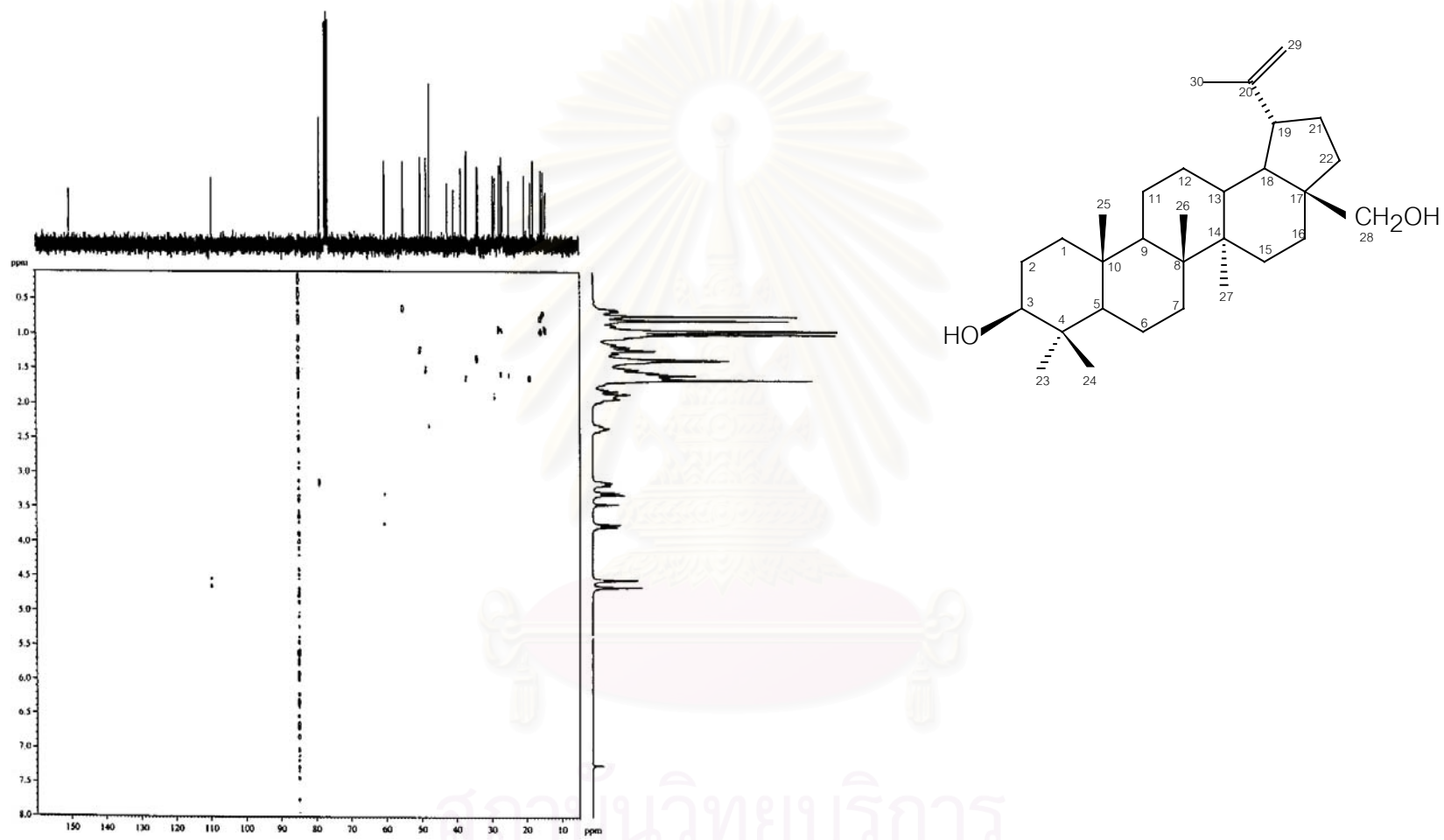


Figure 27a. The 75 MHz ^1H - ^{13}C HETCOR NMR spectrum of compound DG4 (in CDCl_3)

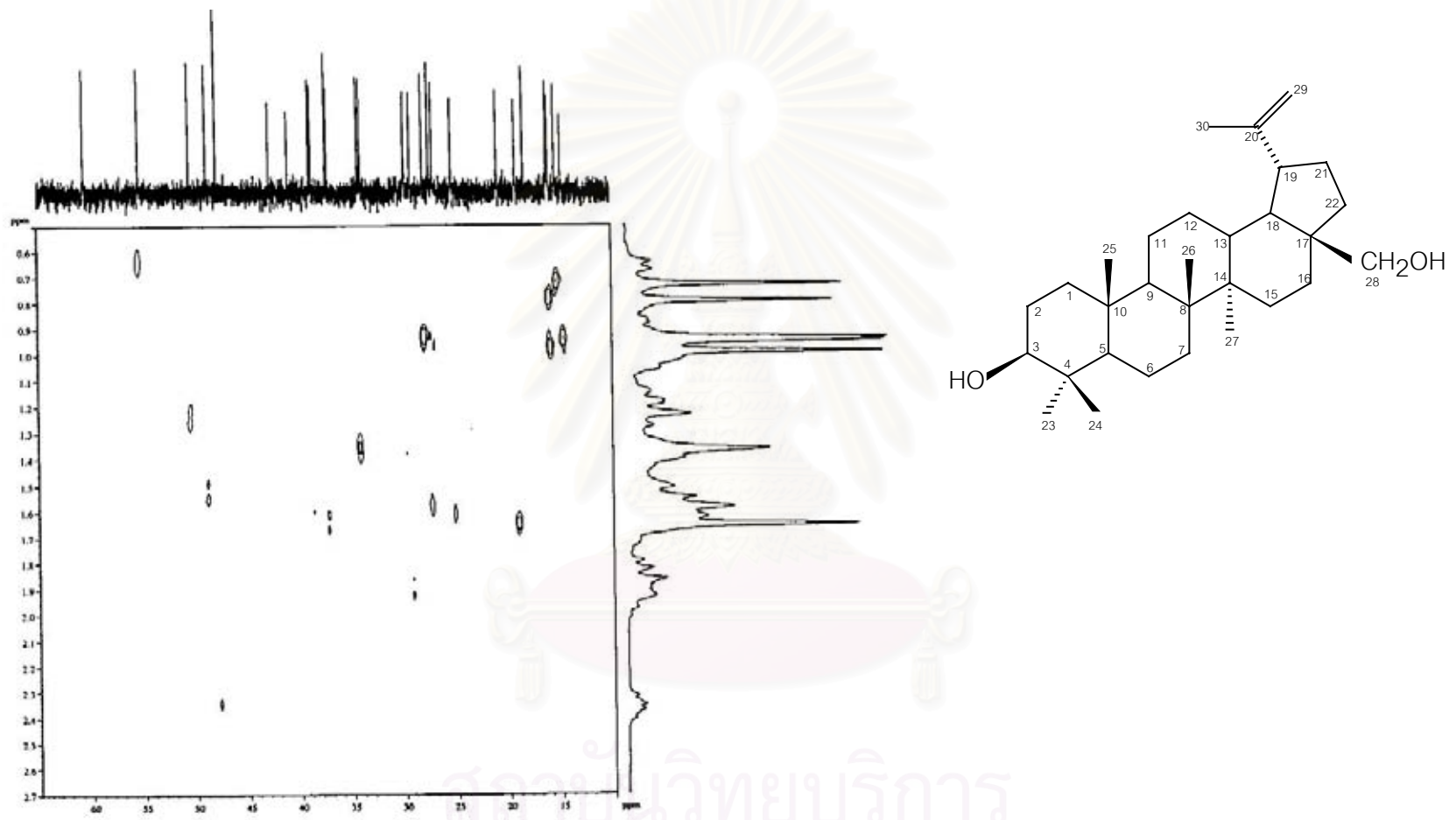


Figure 27b. The 75 MHz ^1H - ^{13}C HETCOR NMR spectrum of compound DG4 (expanded)

5. Identification of Compound DG5

Compound DG5 was recrystallized as colorless prisms from hexane (108.2 mg, 0.02 % yield). The compound gave purple color to Liebermann-Burchard reagent, suggesting its triterpenoid nature. The base peak at m/z 248 in the EIMS (Figure 28) is the characteristic feature of a C-12 unsaturated triterpenoid with oleanane or ursane skeleton containing carboxylic group in ring D or E (Ogunkoya, 1981). This peak resulted from cleavage through retro-Diels-Alder reaction. The further loss of two methyl groups produced the mass fragment peak at m/z 219, while the loss of the carboxylic group led to the peak at m/z 203. The peak at m/z 189 was produced by the loss of water from the other retro-Diels-Alder fragment (Scheme 10). The IR spectrum of DG5 (Figure 29) displayed the carbonyl band at 1694 cm^{-1} and a broad band at 3417 cm^{-1} , indicating the presence of a hydroxyl substituent.

The $^1\text{H-NMR}$ and $^1\text{H-}^1\text{H COSY}$ spectra (Figures 30, 31) exhibited signals due to two secondary methyl (δ 0.80 and 0.90 ppm; *d*) and five tertiary methyls (δ 0.66, 0.74, 0.85, 0.90 and 1.03 ppm; *s*), suggesting that DG5 is an ursane. The most downfield signal at δ 5.12 (*t*, $J = 3.4\text{ Hz}$) ppm, represents H-12 of a C-12 unsaturated triterpenoid. The proton signal at δ 2.99 (*dd*, $J = 5.2, 10.1\text{ Hz}$) ppm confirmed the presence of a hydroxyl group substituent.

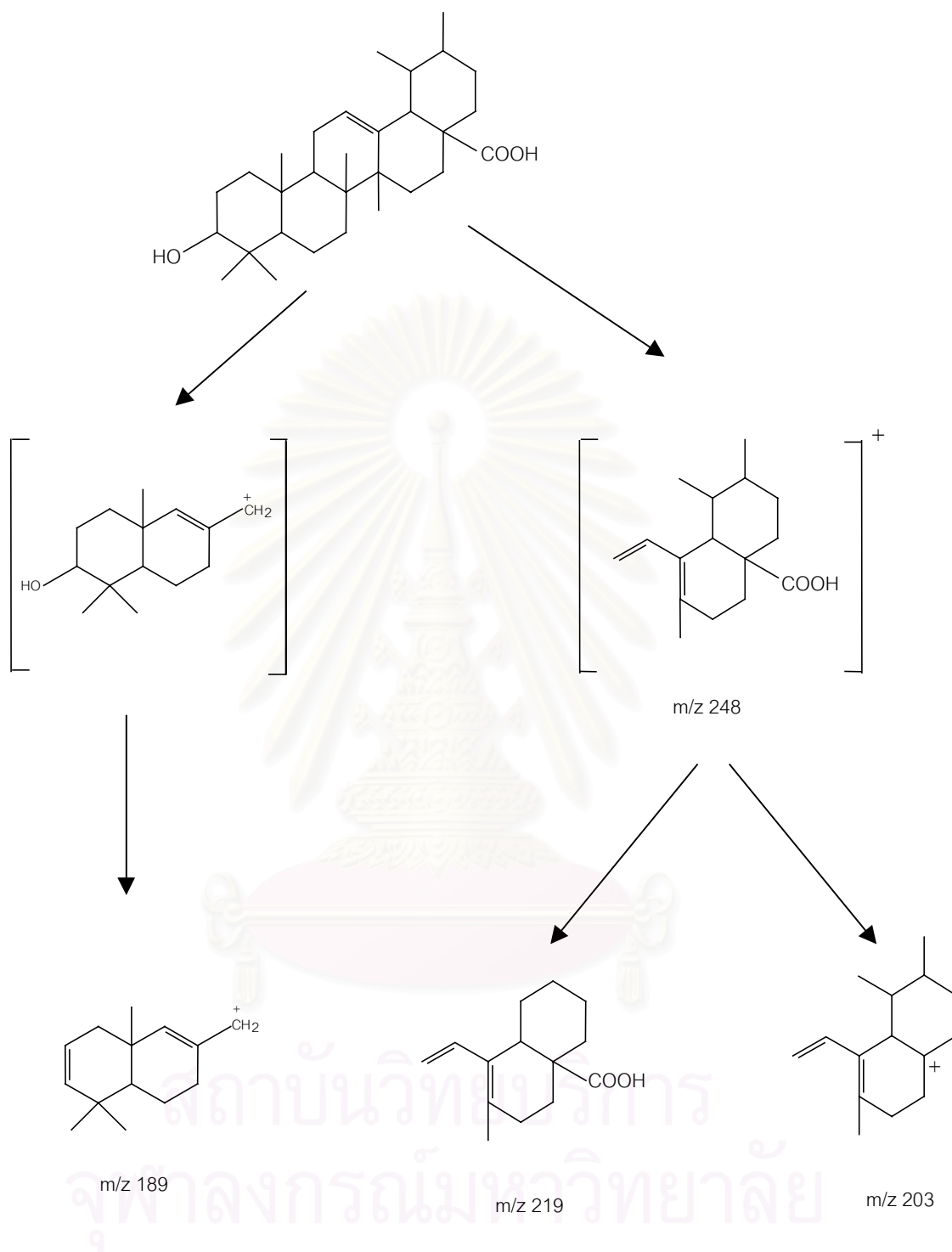
The $^{13}\text{C-NMR}$ spectrum of compound DG5 (Figure 32) showed 30 carbon signals. The DEPT and HETCOR (Figures 33, 34) experiments were employed to classify these signals into seven methyl carbons at δ 15.2, 16.1, 16.9, 17.0, 21.0, 23.3 and 28.2 ppm, nine methylene carbons at δ 18.0, 22.8, 23.8, 26.9, 27.5, 30.2, 32.7, 36.3 and 38.2 ppm, seven methine carbons at δ 38.4, 38.9, 47.0, 52.4, 54.8, 76.8 and 124.6 ppm and seven quaternary carbons at δ 36.5, 38.5, 39.1, 41.6, 46.8, 138.2 and 178.3 ppm. The most downfield carbon signal at δ 178.3 ppm confirmed the presence of a carboxylic group in the molecule of this compound.

Almost all ^{13}C -NMR data of DG5 were found to be in agreement with the data of ursolic acid, reported by Lin, *et al.* (1987), except for the assignments of signal for C-11 and C-29 at δ 22.8 and 17.0 ppm (DG5) instead of δ 17.1 and 23.2 ppm (reported values), respectively. However, the assignments for C-11 and C-29 of DG5 were found to be in agreement with the reported data of methyl ursolate (δ 23.3 ppm for C-11 and δ 16.9 ppm for C-29) (Mahato and Kundu, 1994). In addition, the DEPT experiment of DG5 also pointed out that the carbon signal at δ 17.1 and δ 22.8 ppm are due to methyl (C-29) and methylene (C-11) carbons, respectively.

According to all information mentioned above, DG5 was proposed as a C-12 unsaturated triterpenoid of the ursane type. Comparison of ^{13}C -NMR data of DG5 with those previously reported for ursolic acid (Lin, 1987; Mahato, 1994) a known urs-12-ene, indicated the structures of both compounds to be identical. The ^1H and ^{13}C -NMR assignments of DG5 and the reported ^{13}C -NMR data of ursolic acid are shown in Table 19.

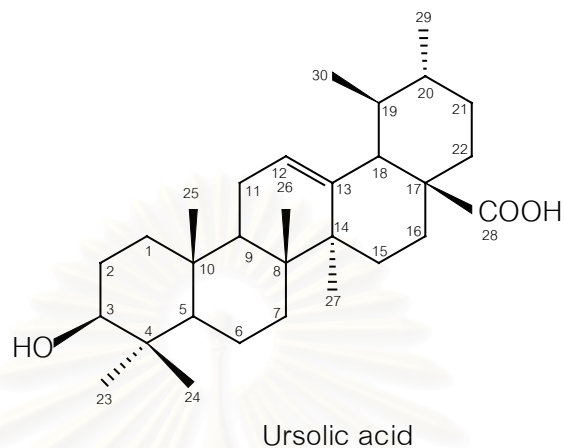


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Scheme 10. Mass fragmentation of compound DG5

Therefore, DG5 was concluded to be ursolic acid, the structure of which is show below.



Ursolic acid was previously isolated from several species of ebenaceous plants, i.e. *Diospyros ferea* (Bhakumi, *et al.*, 1971), *D. melanonilau* (Singh and Prakash, 1998), *D. melanoxylon* (Sankaram and sidhu, 1964). This compound has been reported as possessing antimycobacterial (Cantrell, *et al.*, 2001), anti-inflammatory (Shimizu, *et al.*, 1986), and antiulcer (Gupta, *et al.*, 1981) activities.

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Table 19. ^1H and ^{13}C -NMR assignments of compound DG5 (in $\text{DMSO-}d_6$) and the reported ^{13}C -NMR data of ursolic acid (in $\text{pyridine-}d_5$)

position	Compound DG5		Ursolic acid
	δ H (ppm)	δ C (ppm)	δ C (ppm)
1		38.2	38.7
2		27.0	27.2
3	2.99 (<i>dd</i> , $J = 5.2, 10.1$ Hz)	76.8	78.2
4	-	38.5	38.8
5	-	54.8	55.2
6	-	18.0	18.3
7	-	32.7	33.0
8	-	39.1	39.5
9	-	47.0	47.5
10	-	36.5	36.9
11	-	22.8	17.1
12	5.12 (<i>t</i> , $J = 3.4$ Hz)	124.6	125.2
13	-	138.2	138.3
14	-	41.6	42.0
15	-	27.5	28.2
16	-	23.8	24.2
17	-	46.8	47.5
18	2.10(<i>d</i> , $J = 11.6$ Hz)	52.4	52.7
19	-	38.5	39.1
20	-	38.4	38.8
21	-	30.2	30.7
22	-	36.3	36.7
23	0.88 (<i>s</i>)	28.2	28.0
24	0.86 (<i>s</i>)	15.2	15.7
25	0.67 (<i>s</i>)	16.1	15.4
26	0.74 (<i>s</i>)	16.9	17.0
27	1.03 (<i>s</i>)	23.3	23.5
28	-	178.3	179.9
29	0.80 (<i>d</i> , $J = 6.4$ Hz)	17.0	23.2
30	0.89 (<i>d</i> , $J = 8.9$ Hz)	21.0	21.2

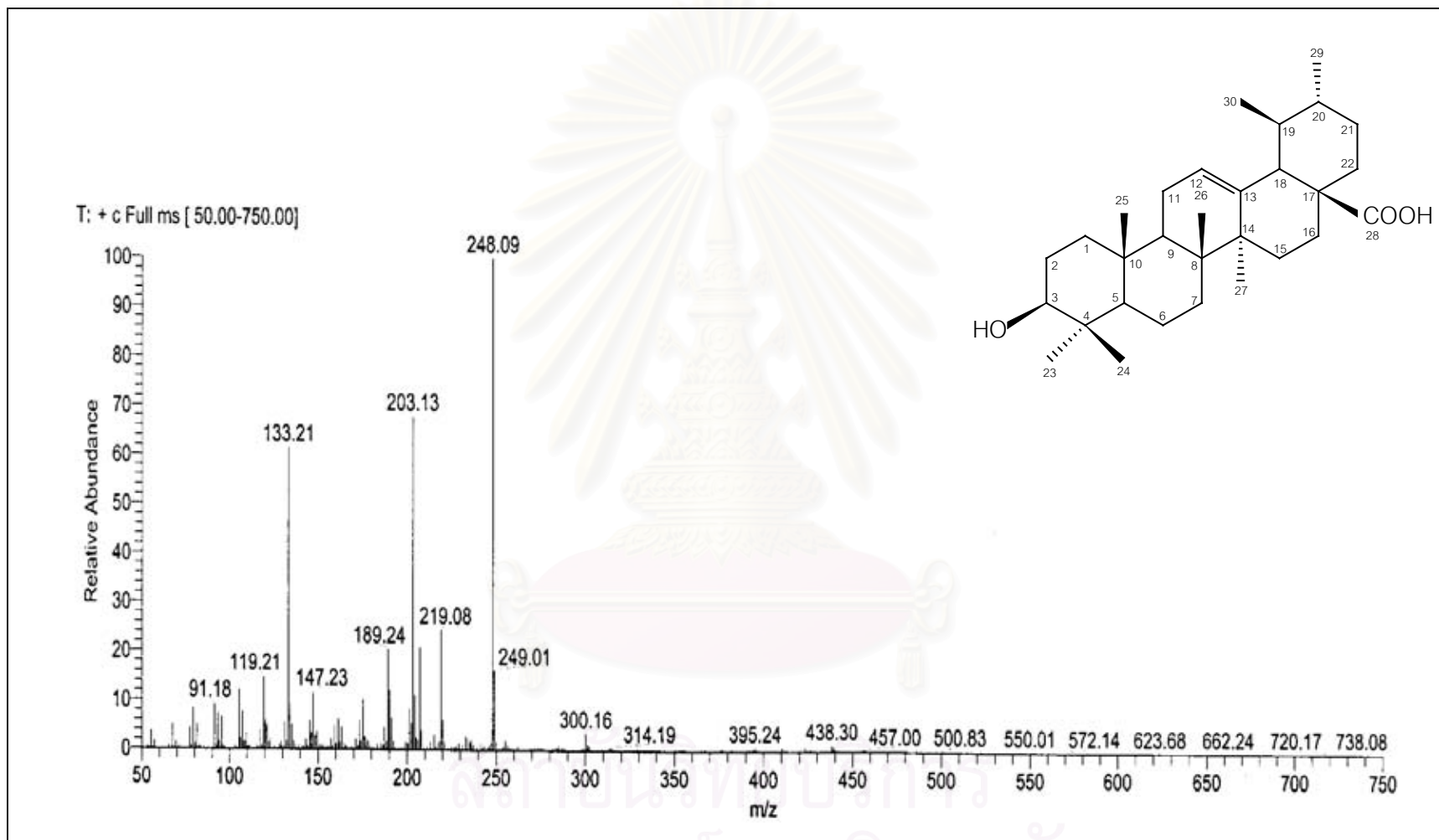


Figure 28. EIMS of compound DG5

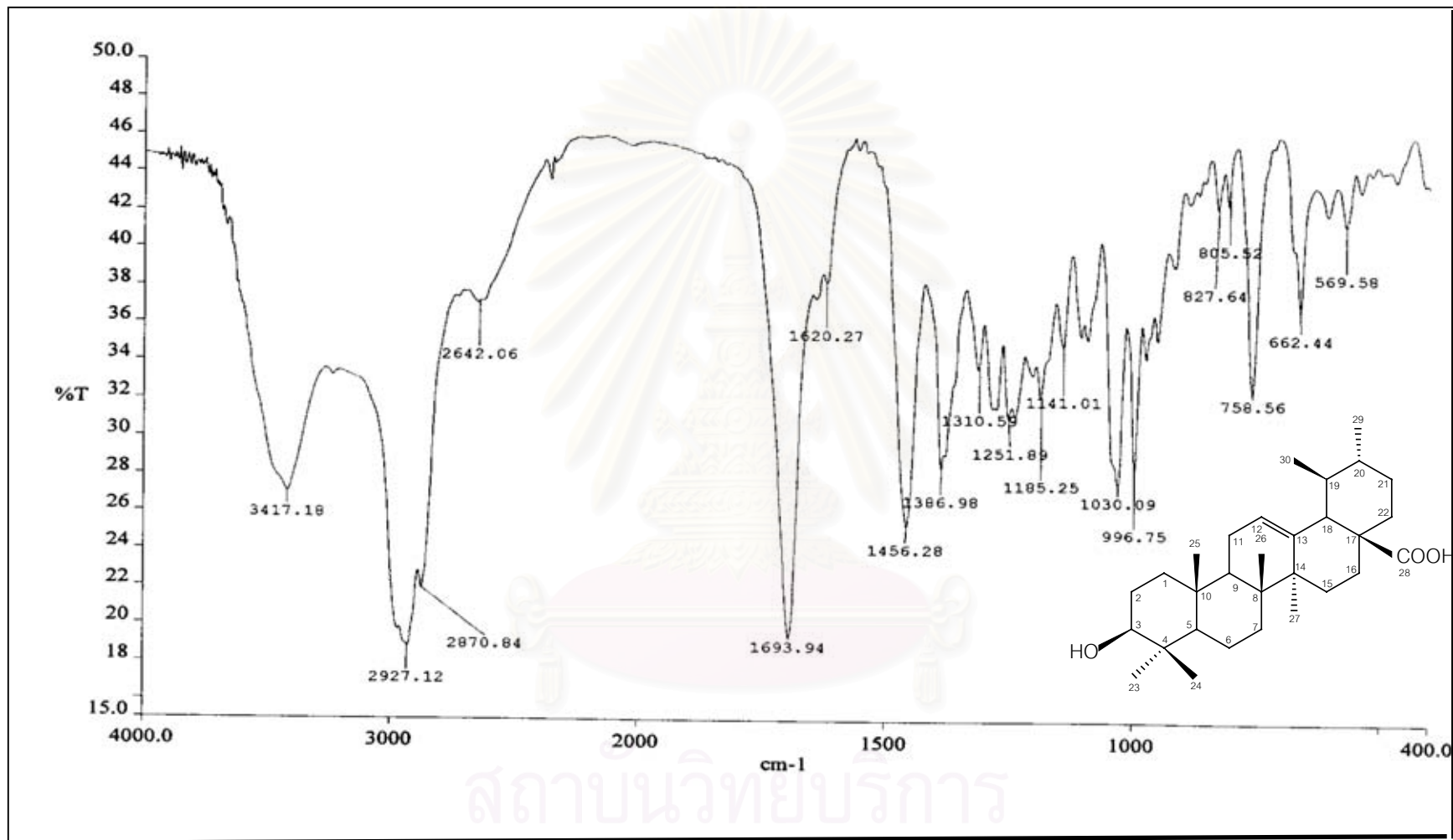


Figure 29. IR spectrum of compound DG5

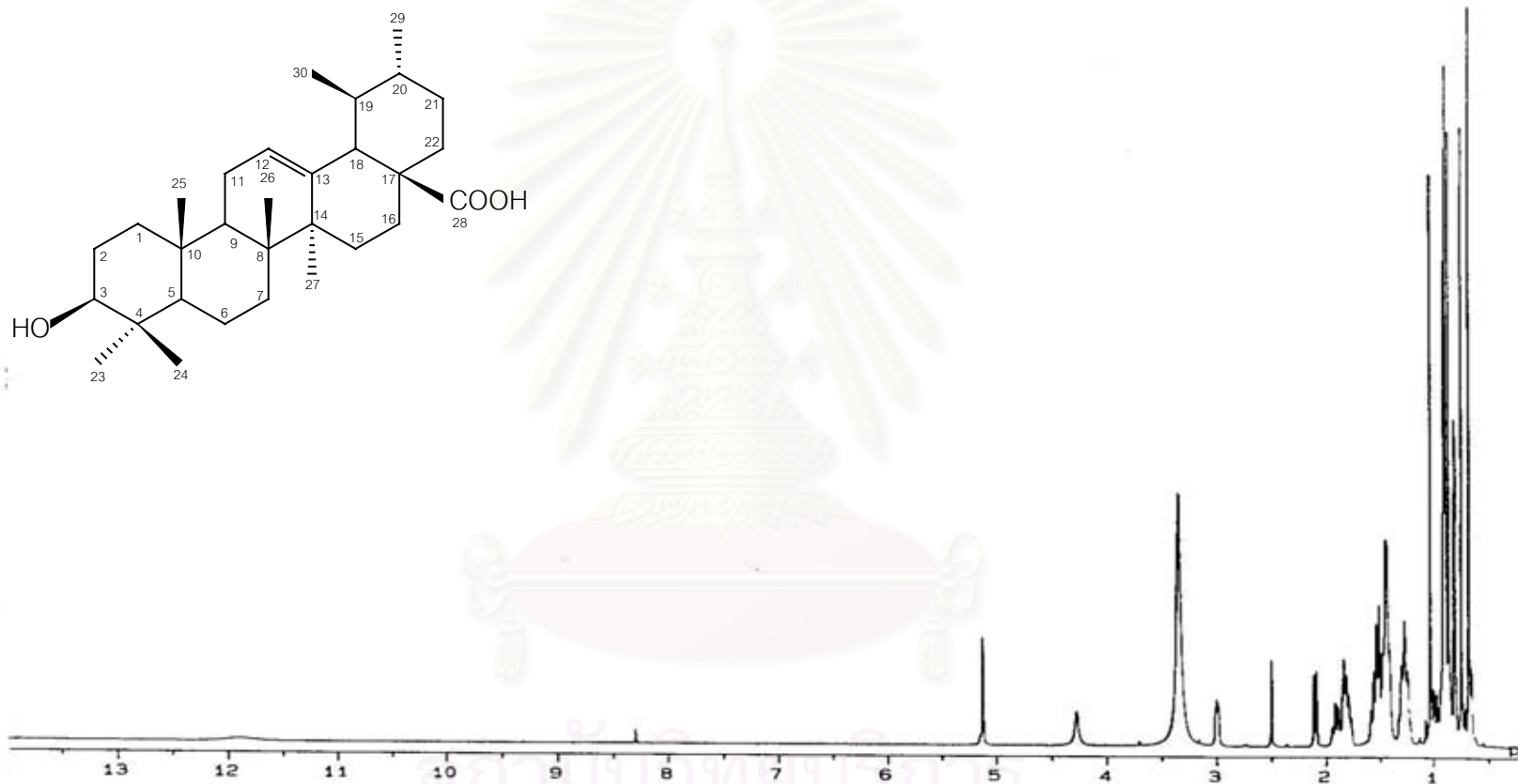
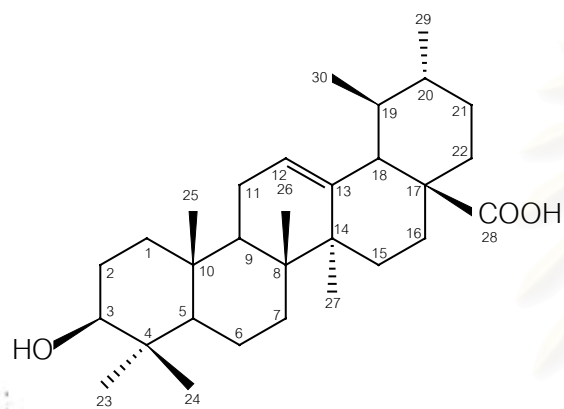


Figure 30a. The 500 MHz ^1H -NMR spectrum of compound DG5 (in DMSO)

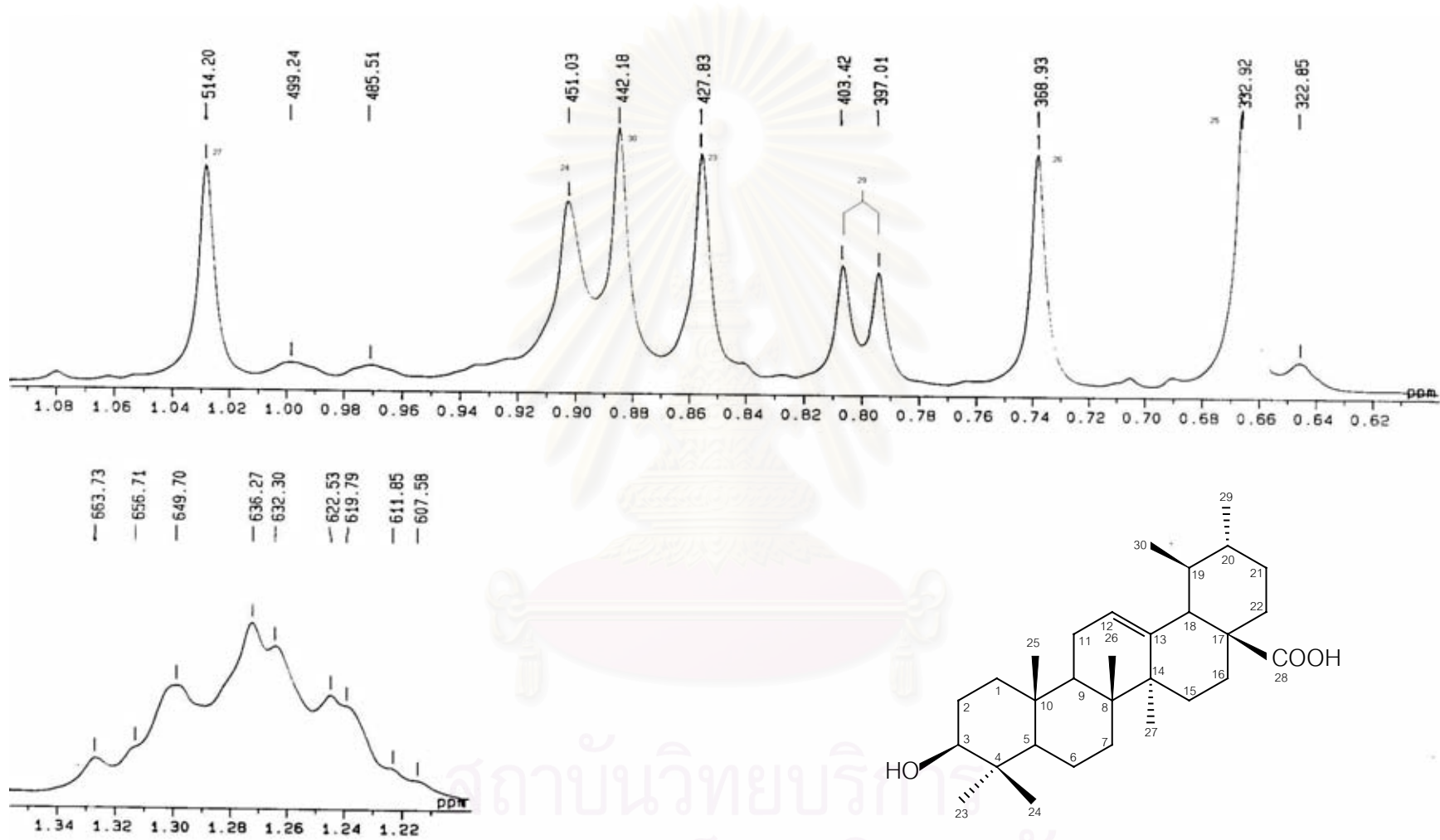


Figure 30b. The 500 MHz $^1\text{H-NMR}$ spectrum of compound DG5 (expanded)

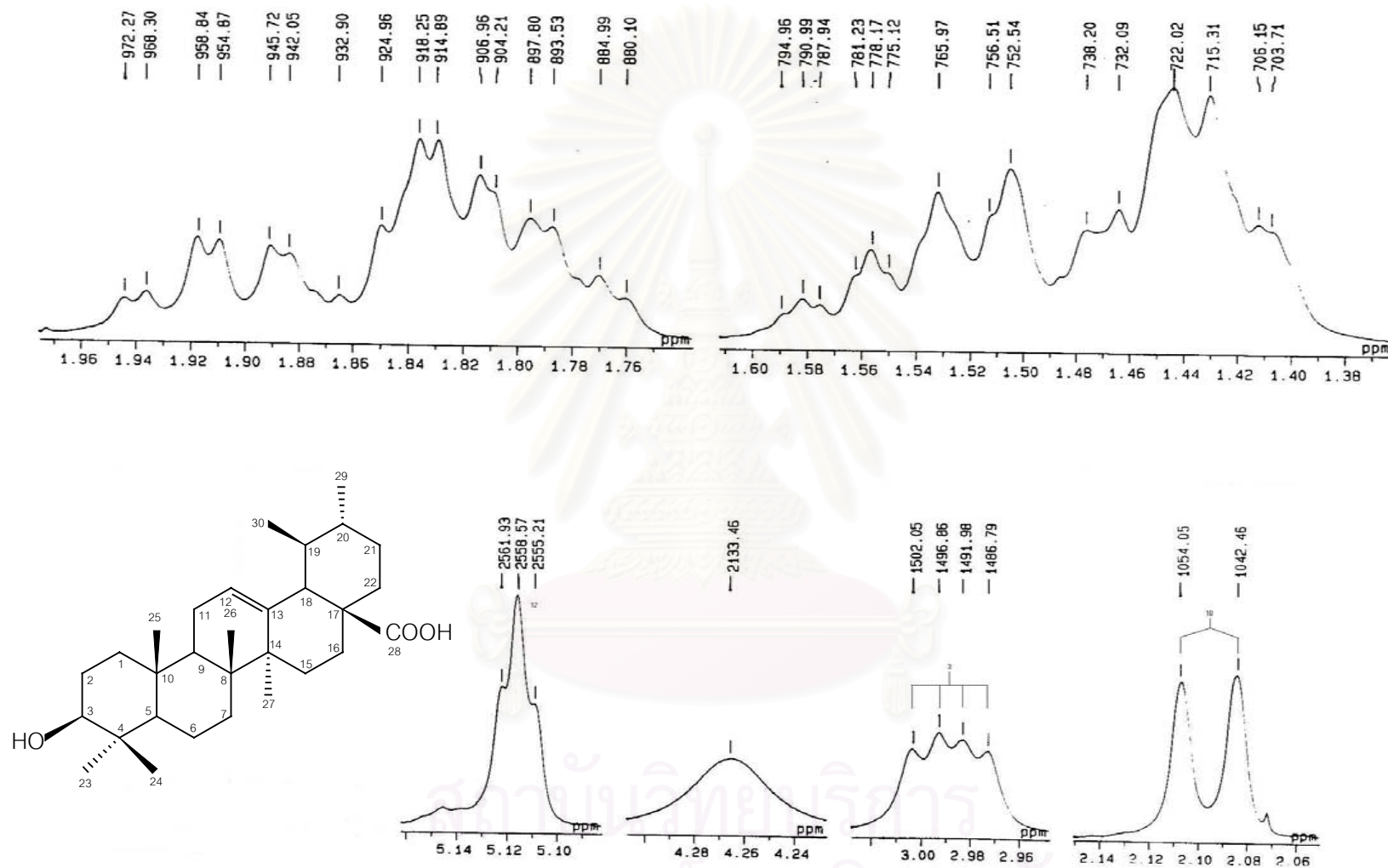


Figure 30c. The 500 MHz $^1\text{H-NMR}$ spectrum of compound DG5 (expanded)

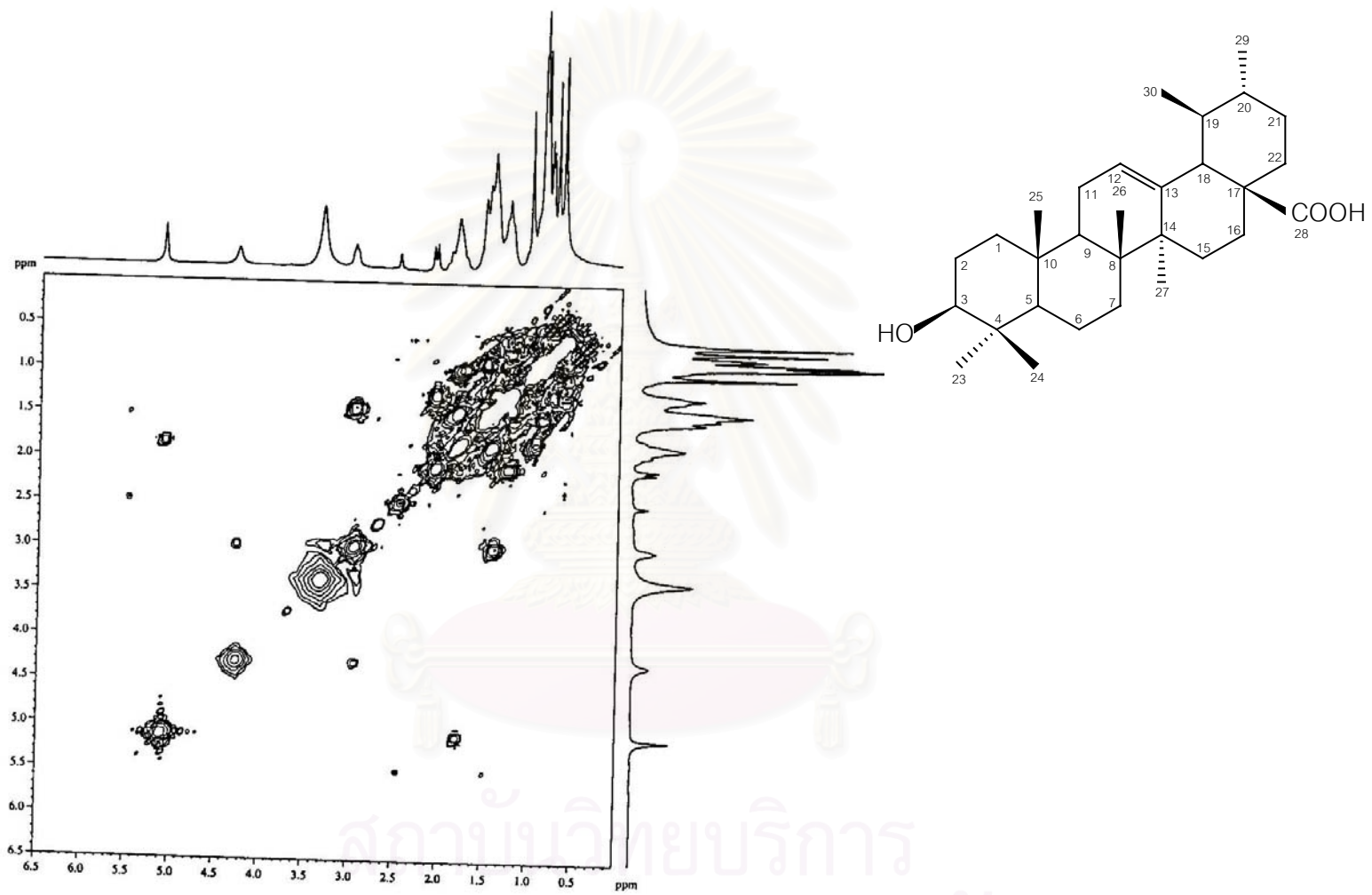


Figure 31. The 300 MHz ¹H-¹H COSY spectrum of compound DG5 (in DMSO)

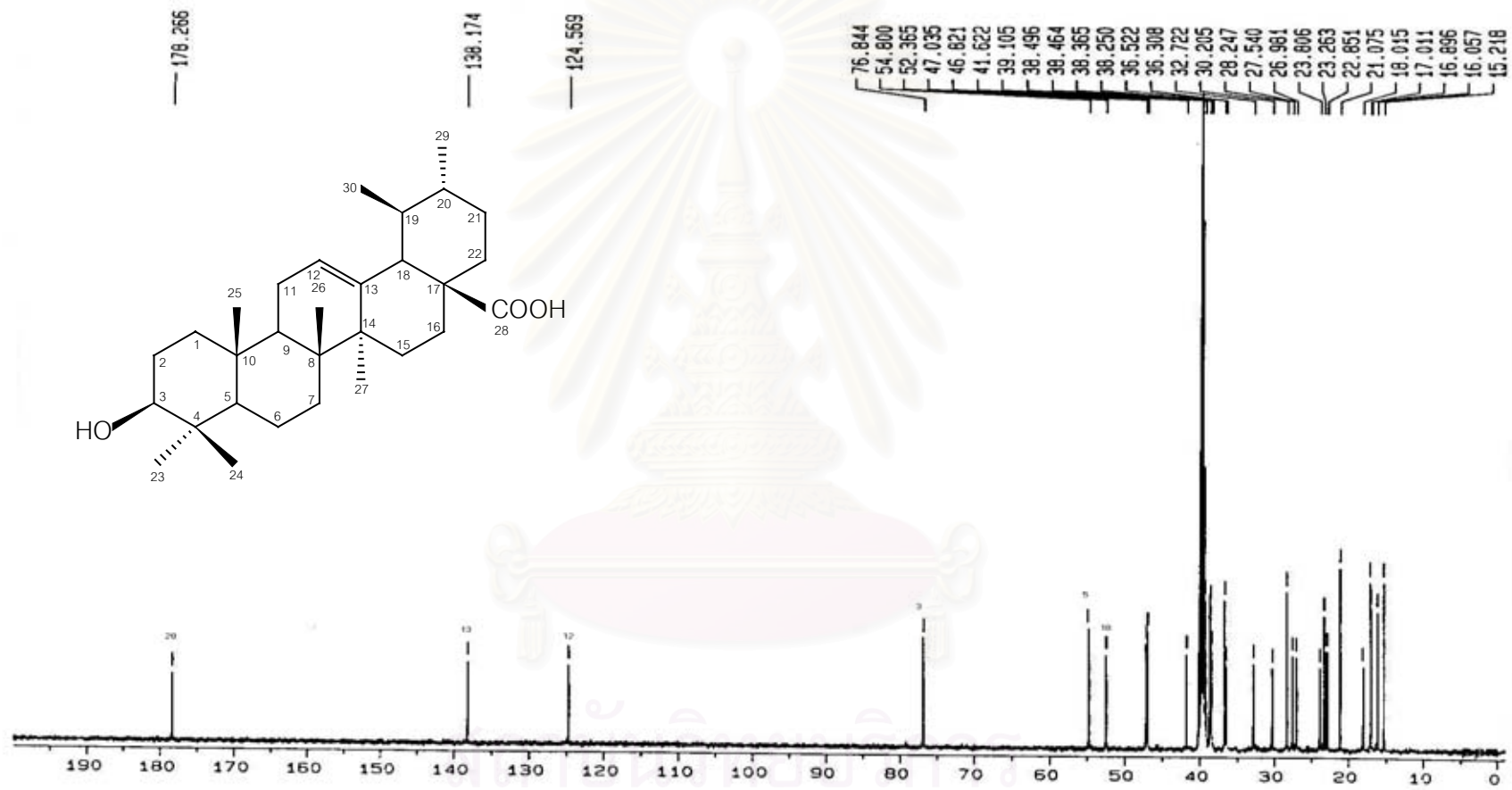


Figure 32a. The 125 MHz ^{13}C -NMR spectrum of compound DG5 (in DMSO)

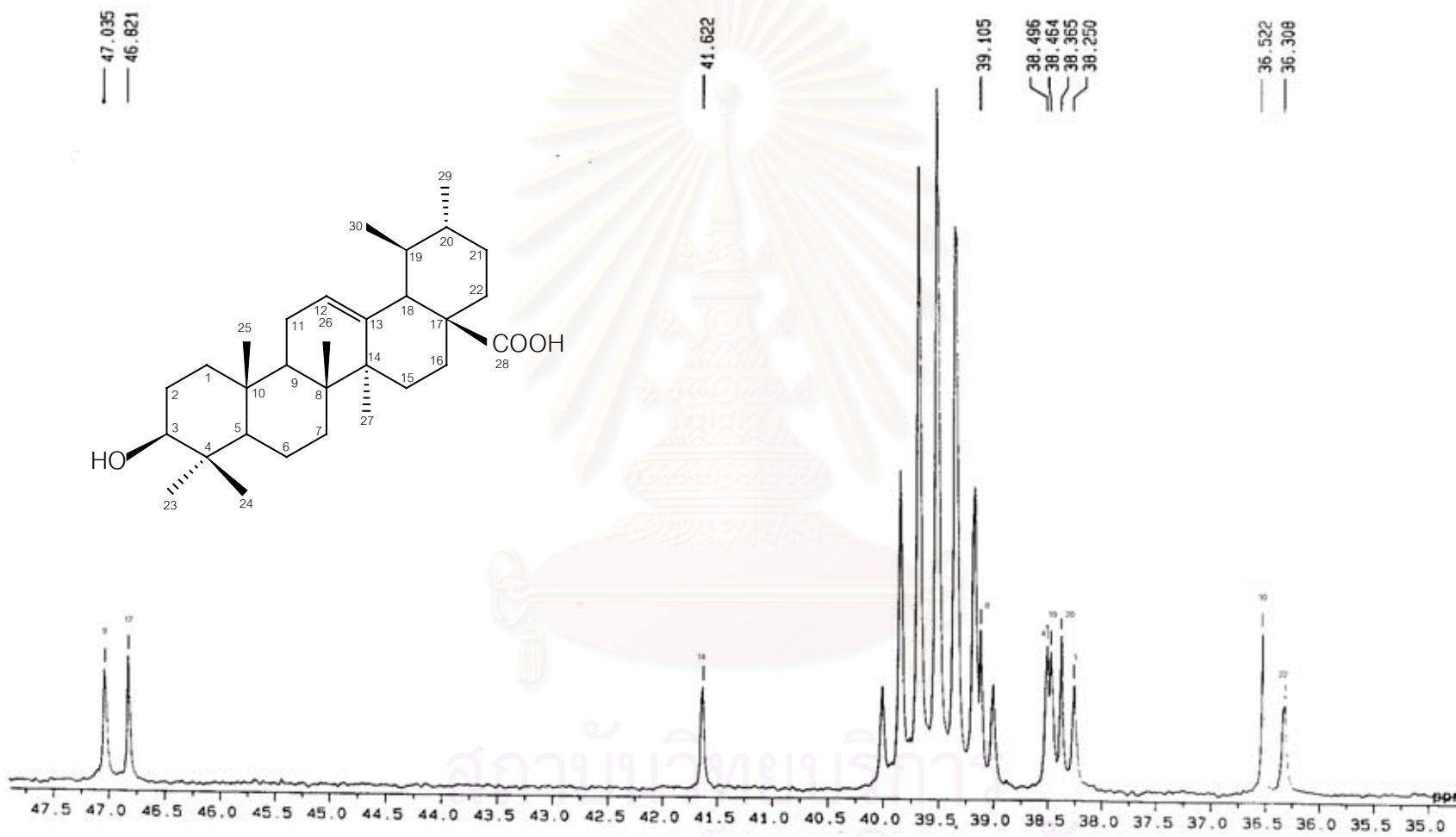


Figure 32b. The 125 MHz ¹³C-NMR spectrum of compound DG5 (expanded)

32.722
30.205
28.247
27.540
26.981
23.806
23.263
22.851
21.075
18.015
17.011
16.896
16.057
15.218

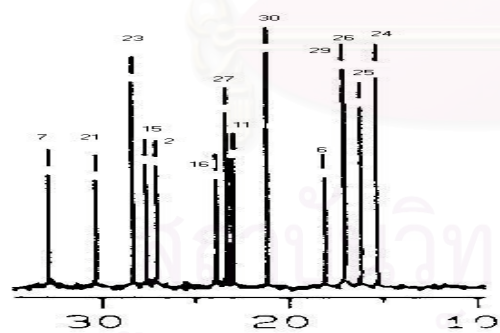
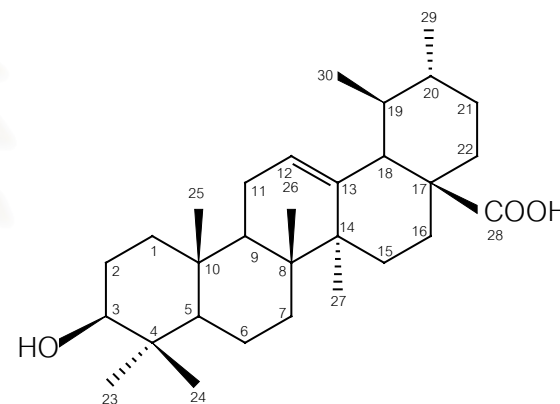


Figure 32c. The 125 MHz ^{13}C -NMR spectrum of compound DG5 (expanded)

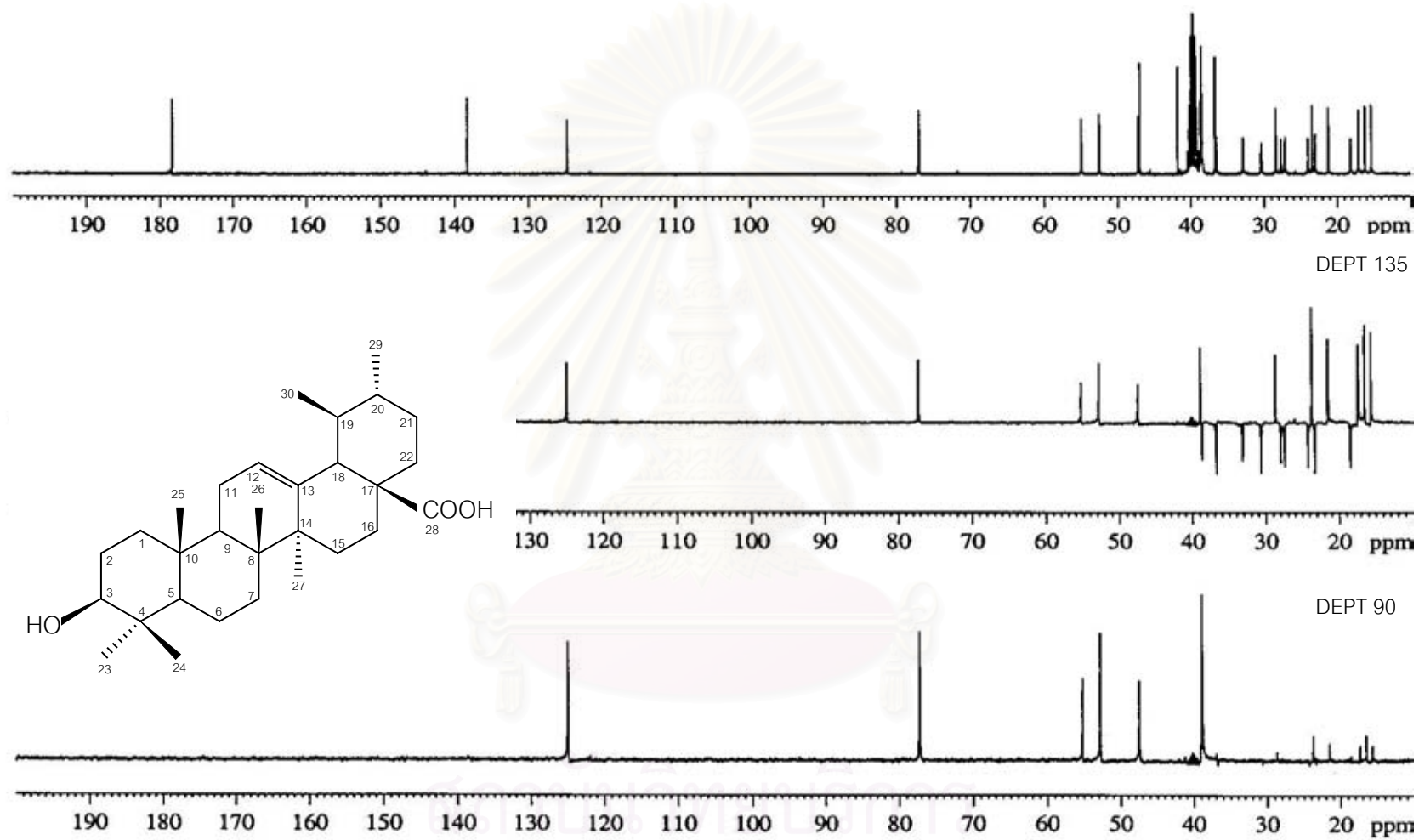


Figure 33a. The 75 MHz ^{13}C -DEPT NMR spectrum of compound DG5 (in DMSO)

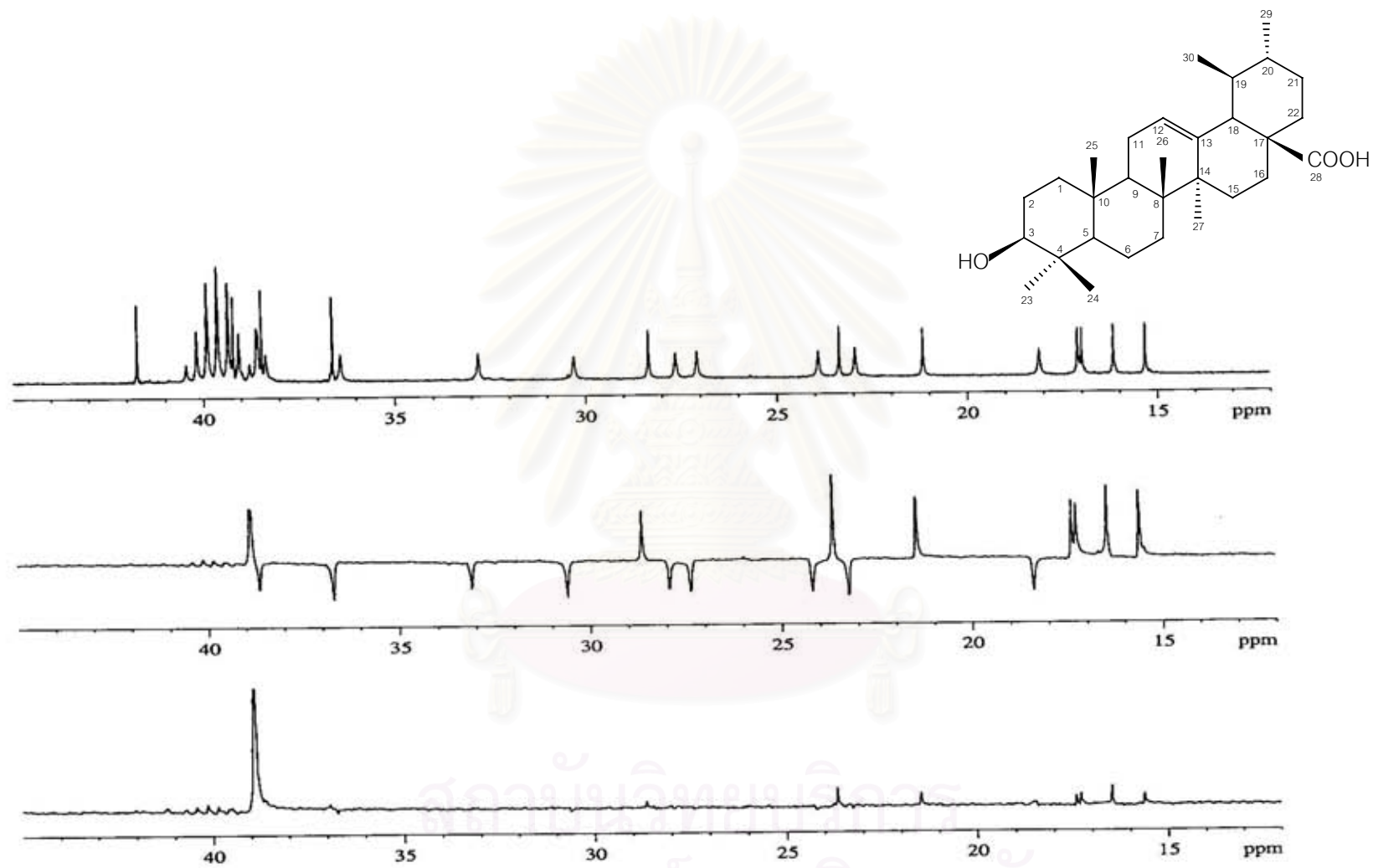


Figure 33b. The 75 MHz ¹³C-DEPT NMR spectrum of compound DG5 (expanded)

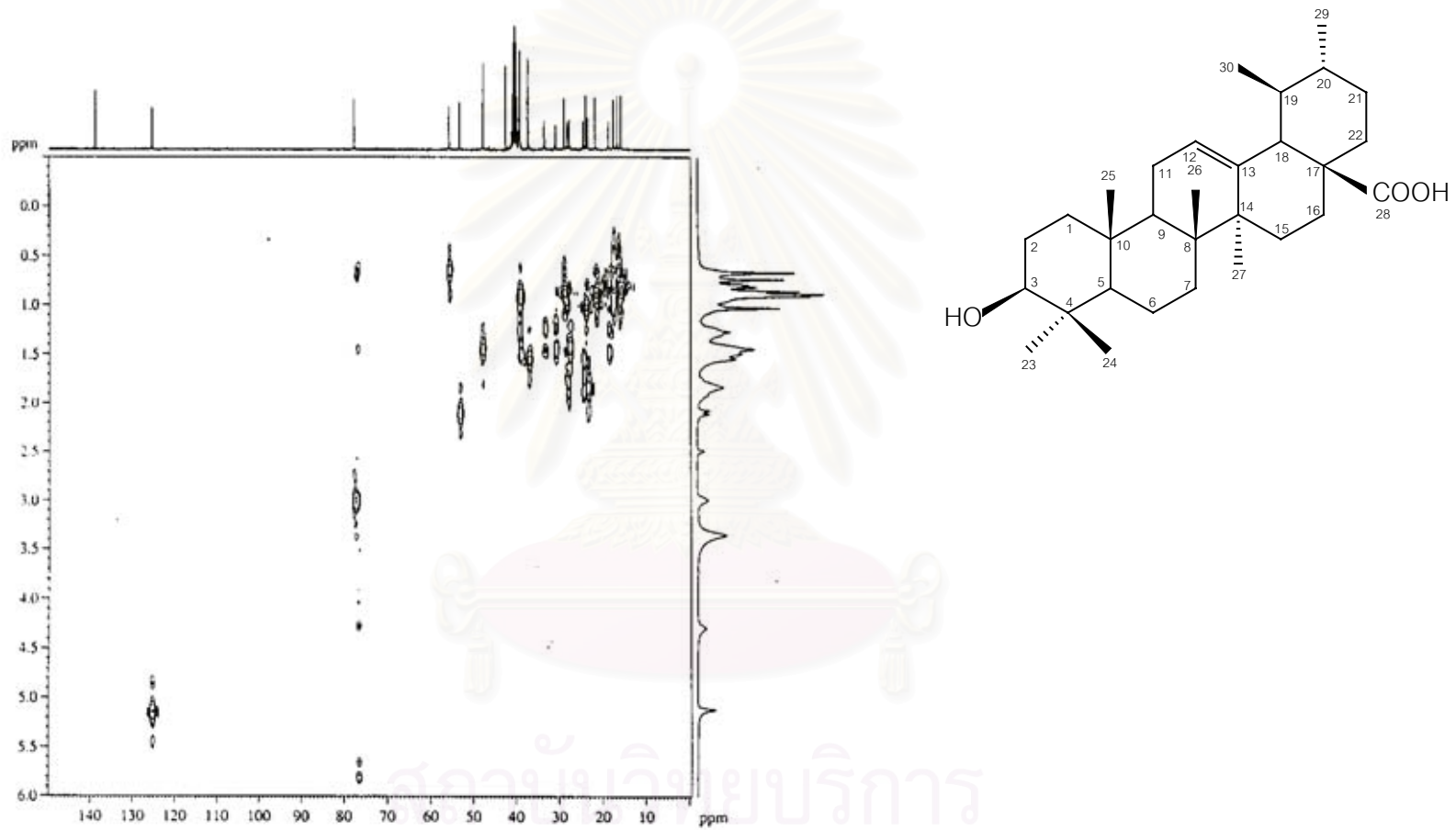


Figure 34a. The 75 MHz ^1H - ^{13}C HETCOR NMR spectrum of compound DG5 (in DMSO)

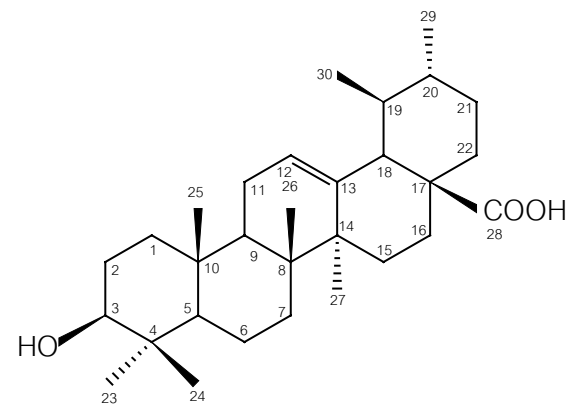
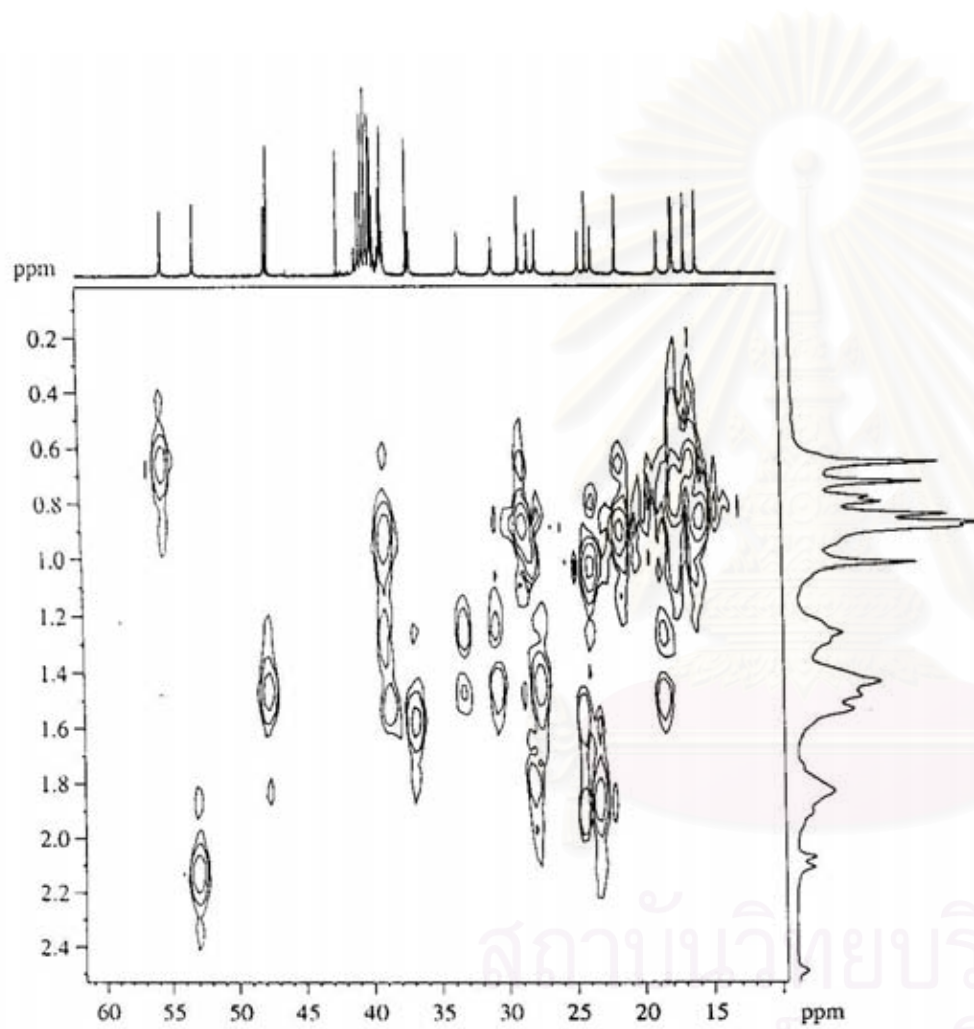


Figure 34b. The 75 MHz ^1H - ^{13}C HETCOR NMR spectrum of compound DG5 (expanded)

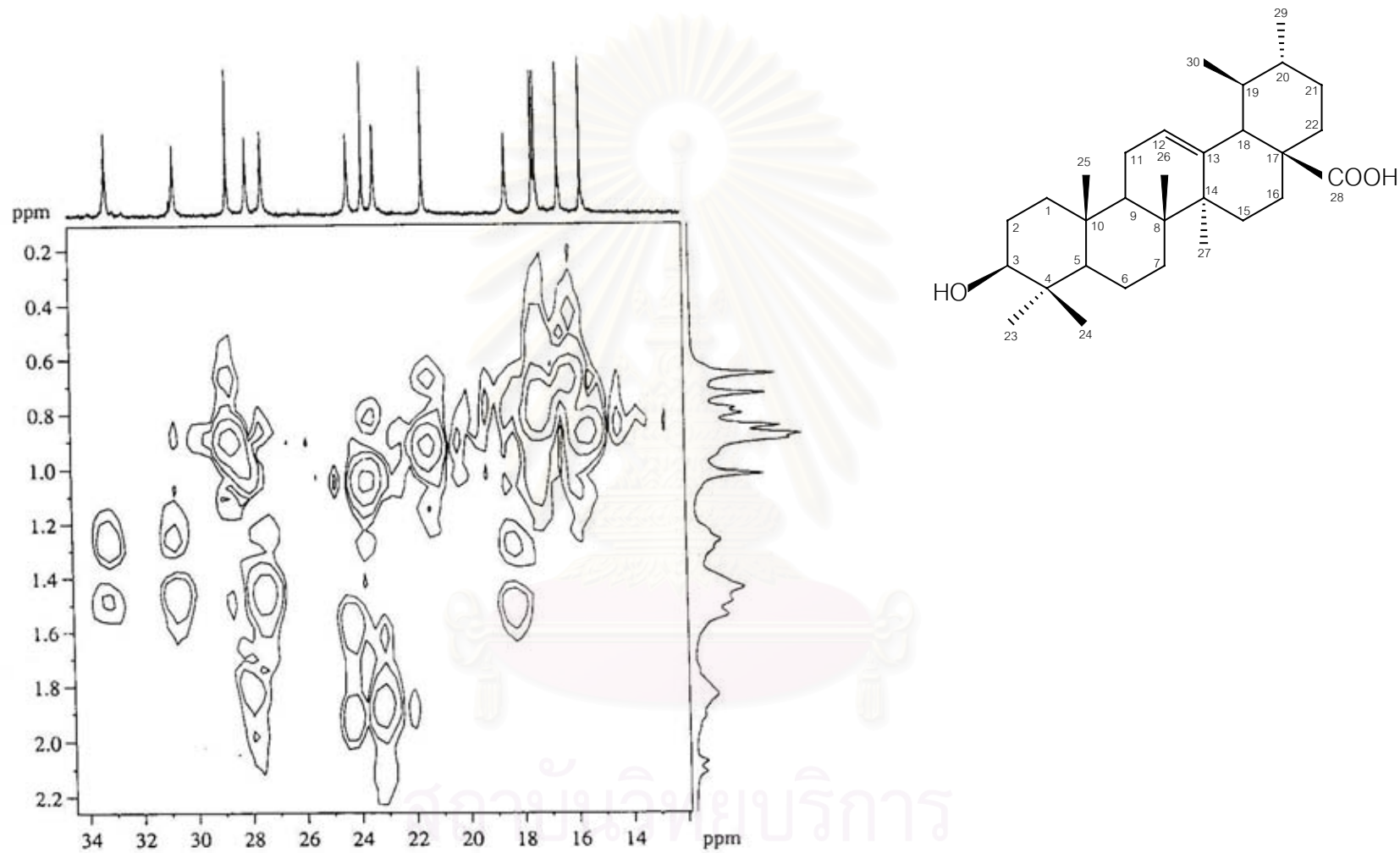


Figure 34c. The 75 MHz ^1H - ^{13}C HETCOR NMR spectrum of compound DG5 (expanded)

6. Identification of Compound DG6

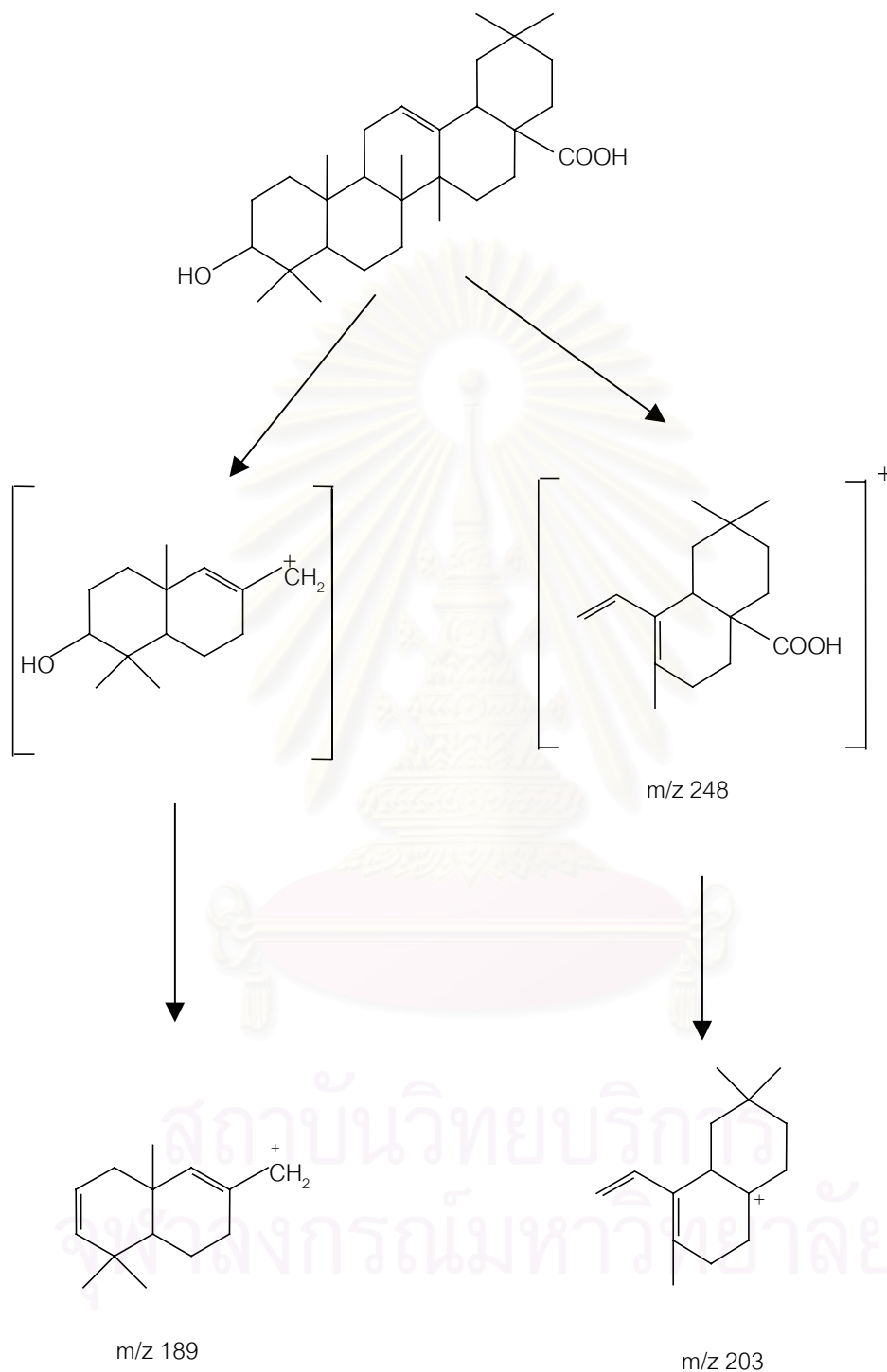
Compound DG6 was recrystallized as colorless needles from methanol (50.4 mg, 0.02% yield). This compound gave purple color to Liebermann-Burchard reagent, suggestive of a triterpenoid. Its EIMS (Figure 35) showed a molecular ion peak at m/z 456 which corresponded to the molecular formula of $C_{30}H_{48}O_3$. The base peak at m/z 248 is the characteristic of a C-12 unsaturated triterpenoid with oleanane or ursane skeleton containing a carboxylic group in ring D or E (Ogunkoya, 1981). The production of this peak as well as the peaks at m/z 203 and m/z 189 could be explained by the same deduction as those of DG5 (Scheme 11). The IR spectrum (Figure 36) of DG6 revealed absorption band at 3431 cm^{-1} (broad), suggesting the presence of a hydroxyl substituent and it also displayed a carbonyl band at 1695 cm^{-1} .

The $^1\text{H-NMR}$ and $^1\text{H-}^1\text{H COSY}$ spectra (Figures 37, 38) of DG6 showed seven singlets of tertiary methyls (δ 0.73, 0.75, 0.88, 0.89, 0.91, 0.96, and 1.11 ppm), suggesting that DG6 is an oleanane. The most downfield signal at δ 5.26 (br. s) ppm, represents H-12 of a C-12 unsaturated triterpenoid. The proton signal at δ 3.20 (*dd*, $J = 4.7, 10.1\text{ Hz}$) ppm confirmed the presence of a hydroxyl substituent.

The $^{13}\text{C-NMR}$ spectrum of DG6 (Figure 39) showed 30 carbon signals. The DEPT and HETCOR experiments (Figures 40, 41) were employed to classify these signals in to those of seven methyl carbons at δ 15.3, 15.5, 17.1, 23.6, 25.9, 28.1 and 33.0 ppm, ten methylene carbons at δ 18.3, 22.9, 23.4, 27.2, 27.7, 32.4, 32.6, 33.8, 38.4 and 45.8 ppm, five methine carbons at δ 40.9, 47.6, 55.2, 79.0 and 122.6 ppm and eight quaternary carbons at δ 30.6, 37.1, 38.7, 39.2, 41.6, 46.5, 143.6 and 183.6 ppm. The most downfield carbon signal at δ 183.6 ppm confirmed the presence of a carboxylic group in the molecule of this compound.

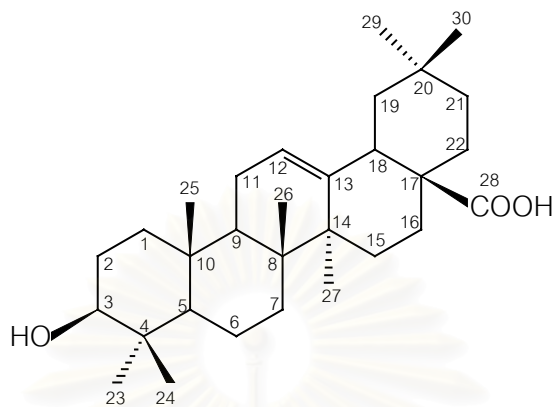
According to all information mentioned above, DG6 was proposed as a C-12 unsaturated triterpenoid of the oleanane type. Comparison of $^{13}\text{C-NMR}$ data of DG6 with the literature value of oleanolic acid (Maillard, Adewunmi and Hostettmann, 1992) indicated that

they are the same compound. The ^{13}C -NMR assignments of DG6 and oleanolic acid together with ^1H -NMR assignment of DG6 are shown in Table 20.



Scheme11. Mass fragmentation of compound DG6

Therefore DG6 was identified as oleanolic acid, the structure of which is shown below.



Oleanolic acid

Oleanolic acid was previously isolated from several species of ebenaceous plants, i.e. *Diospyros eben* (Musgrave and Skoyles, 1974), *D. montana* (Musgrave and Skoyles, 1974), *D. peregrina* (Gupta and Tiwari, 1964b). This compound has been reported as possessing antimycobacterial (Cantrell, *et al.*, 2001) and antiulcer (Gupta, *et al.*, 1981) activities.

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Table 20. ^1H and ^{13}C -NMR assignments of compound DG6 (in CDCl_3) and the reported ^{13}C -NMR data of oleanolic acid (in CDCl_3)

position	Compound DG6		Oleanolic acid
	δ H (ppm)	δ C (ppm)	δ C (ppm)
1	-	38.4	38.5
2	-	27.2	27.4
3	3.20 (<i>dd</i> , $J= 4.7, 10.1$ Hz)	79.0	78.7
4	-	38.7	38.7
5	-	55.2	55.2
6	-	18.3	18.3
7	-	32.6	32.6
8	-	39.2	39.3
9	-	47.6	47.6
10	-	37.1	37.0
11	-	23.4	23.1
12	5.26 (<i>br. s</i>)	122.6	122.1
13	-	143.6	143.4
14	-	41.6	41.6
15	-	27.7	27.7
16	-	22.9	23.4
17	-	46.5	46.6
18	2.80 (<i>d</i> , $J=10.2$ Hz)	40.9	41.3
19	1.21-2.02 (<i>m</i>)	45.8	45.8
20	-	30.6	30.6
21	1.21-2.02 (<i>m</i>)	33.8	33.8
22	1.21-2.02 (<i>m</i>)	32.4	32.3
23	0.96 (<i>s</i>)	28.1	28.1
24	0.75 (<i>s</i>)	15.5	15.6
25	0.89 (<i>s</i>)	15.3	15.3
26	0.73 (<i>s</i>)	17.1	16.8
27	1.11 (<i>s</i>)	25.9	26.0
28	-	183.6	181.0
29	0.88 (<i>s</i>)	33.0	33.1
30	0.91 (<i>s</i>)	23.6	23.6

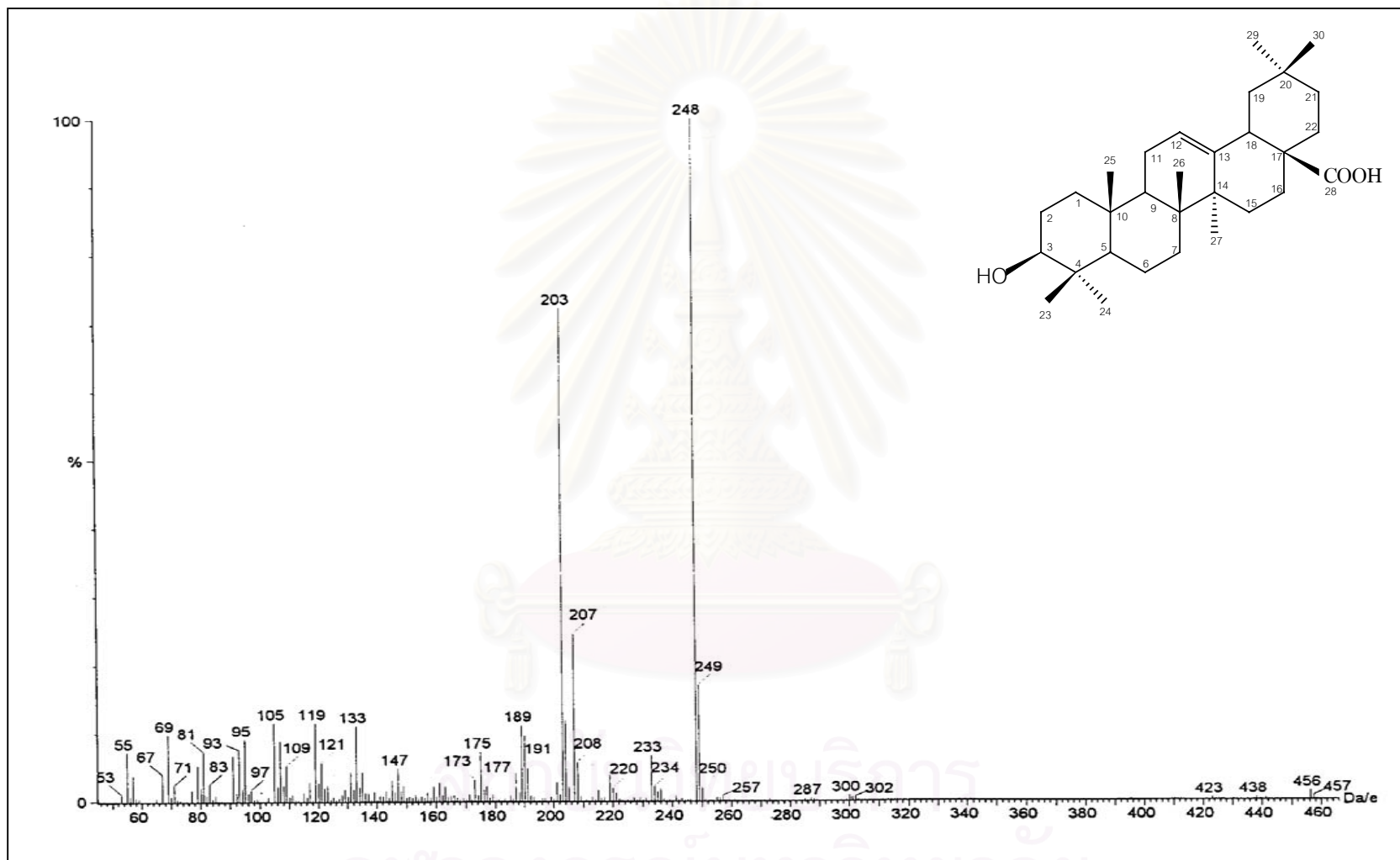


Figure 35. EIMS of compound DG6

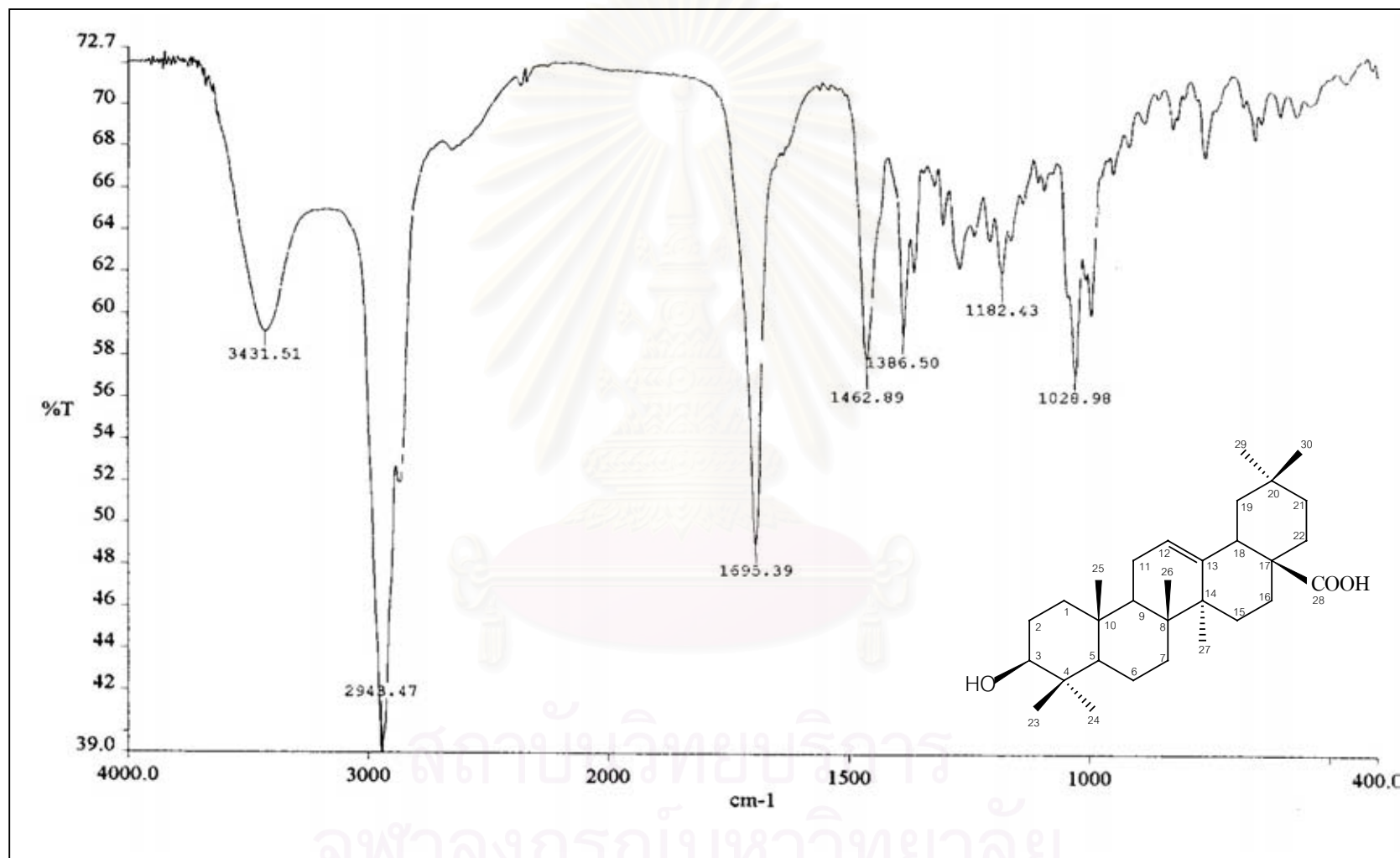


Figure 36. IR spectrum of compound DG6

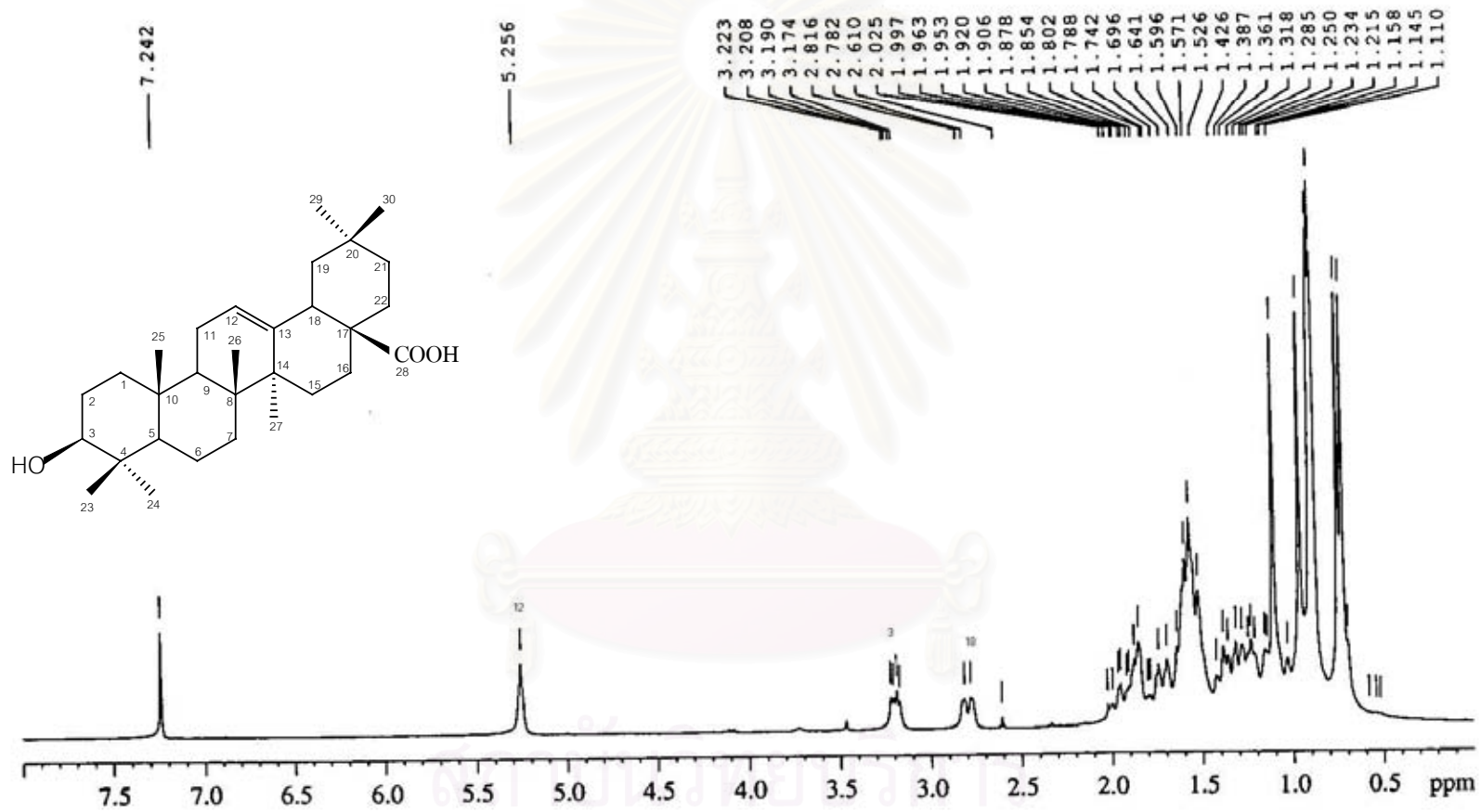


Figure 37a. The 300 MHz ¹H NMR spectrum of compound DG6 (in CDCl₃)

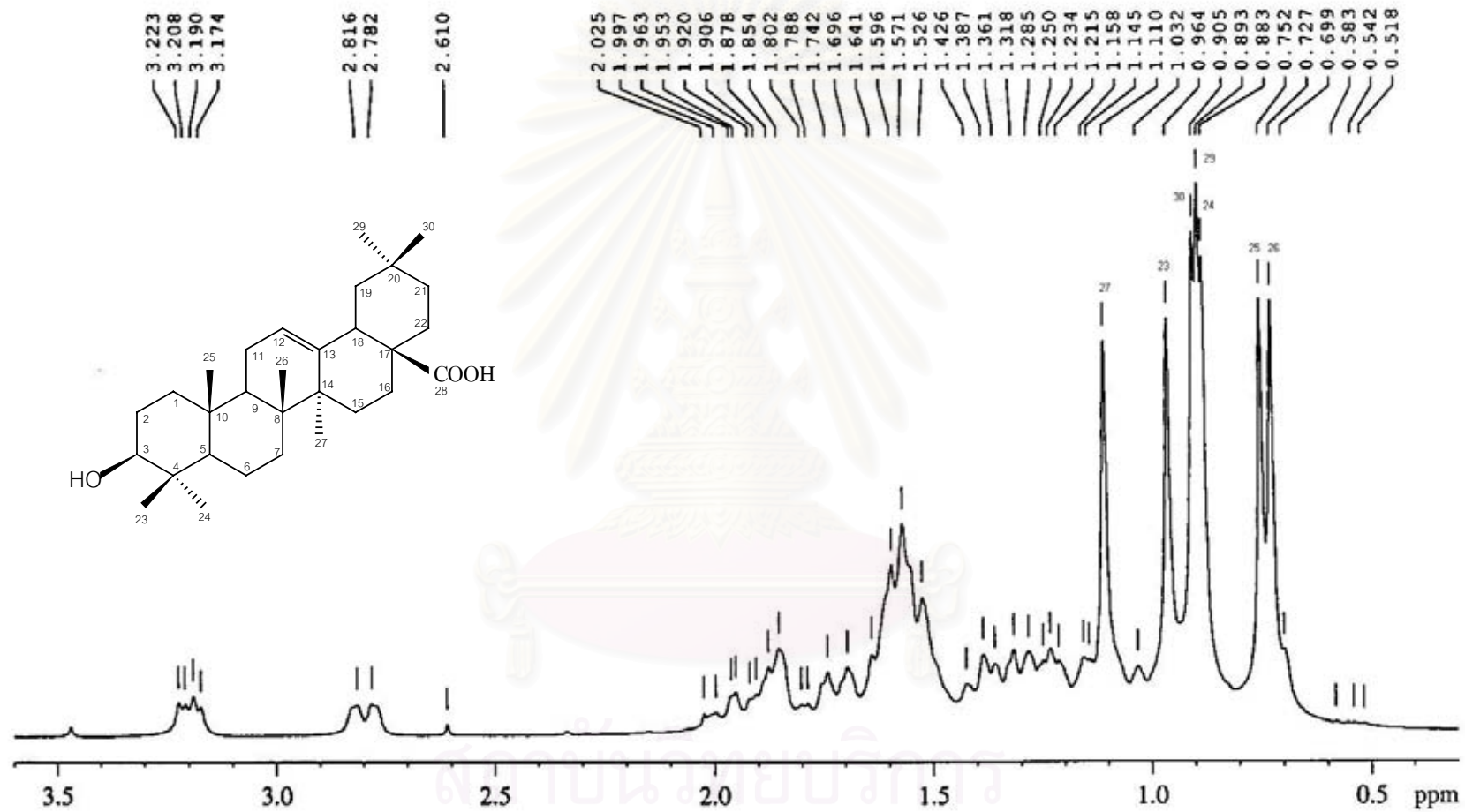


Figure 37b. The 300 MHz ¹H NMR spectrum of compound DG6 (expanded)

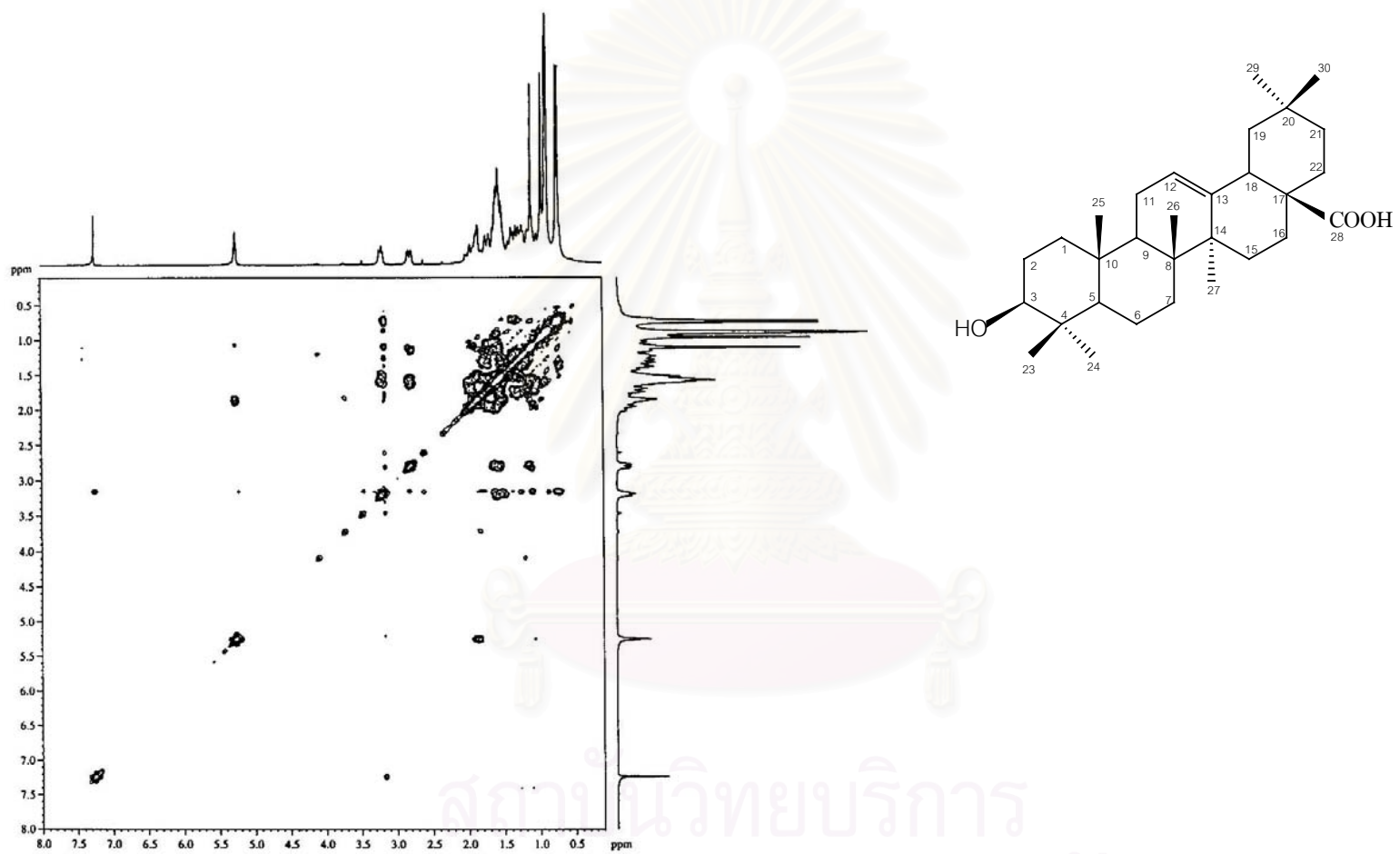


Figure 38a. The 300 MHz ^1H - ^1H COSY spectrum of compound DG6 (in CDCl_3)

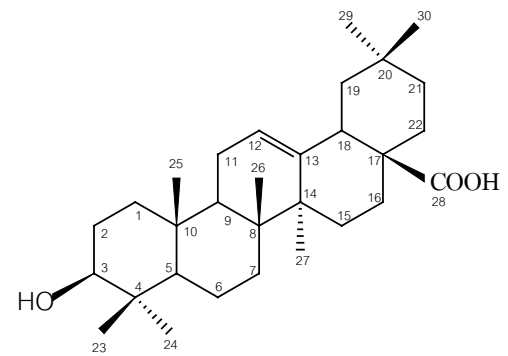
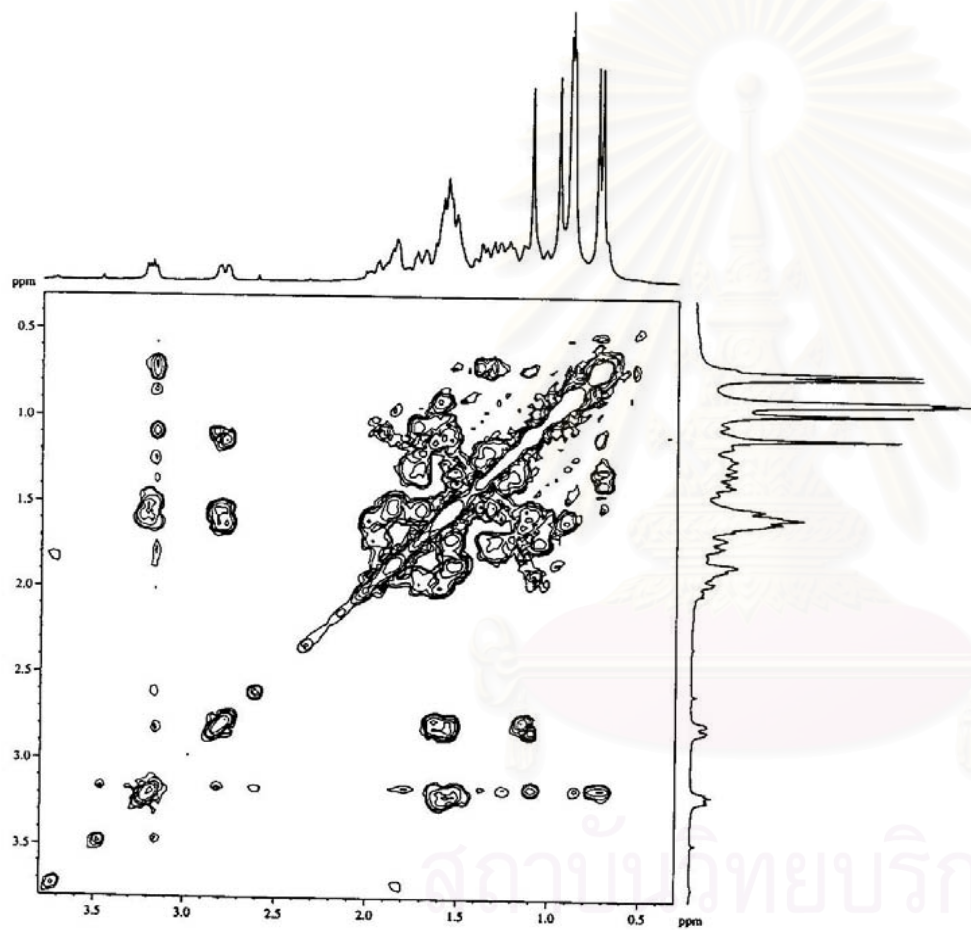
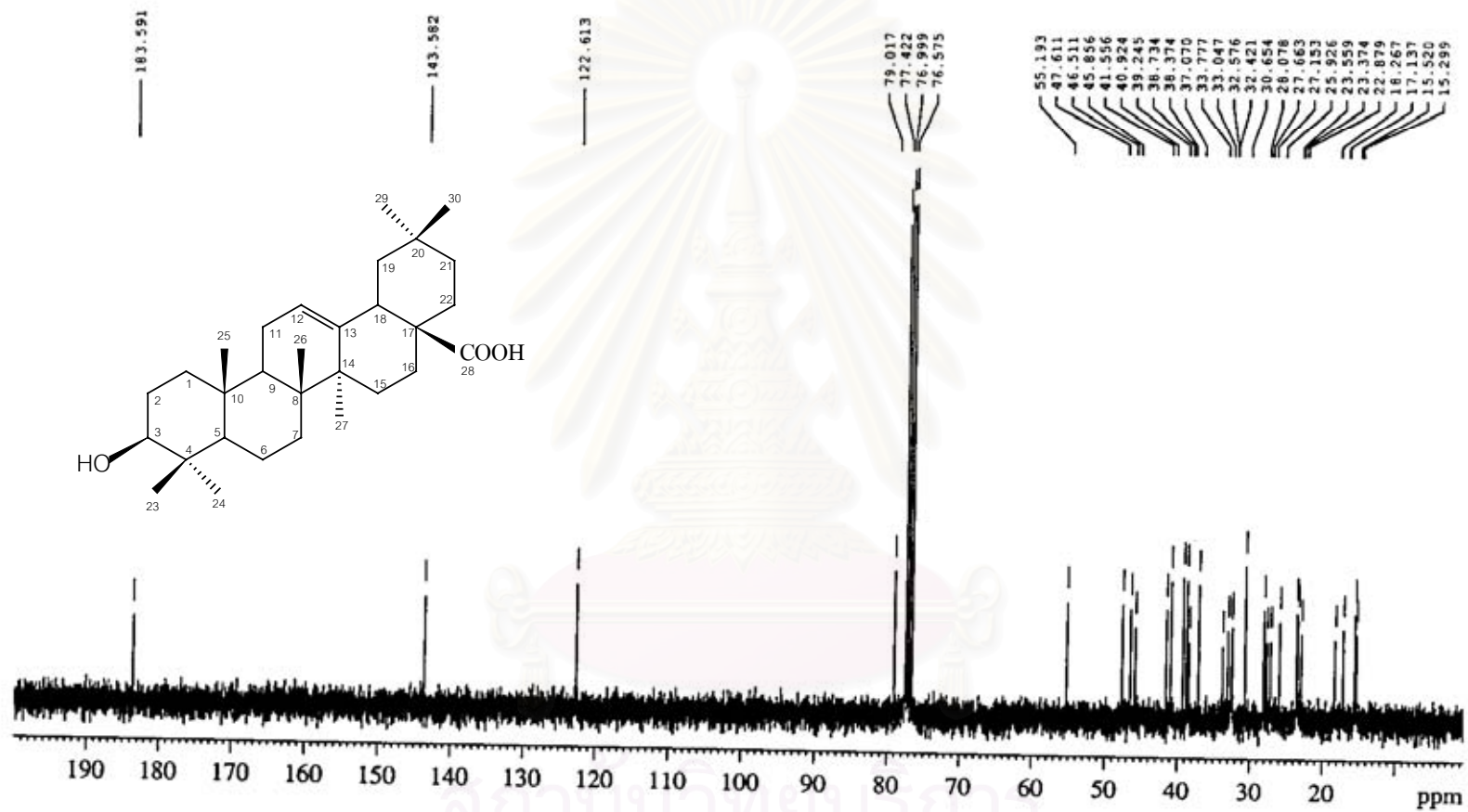


Figure 38b. The 300 MHz ¹H-¹H COSY spectrum of compound DG6 (expanded)



39a. The 75 MHz ^{13}C NMR spectrum of compound DG6 (in CDCl_3)

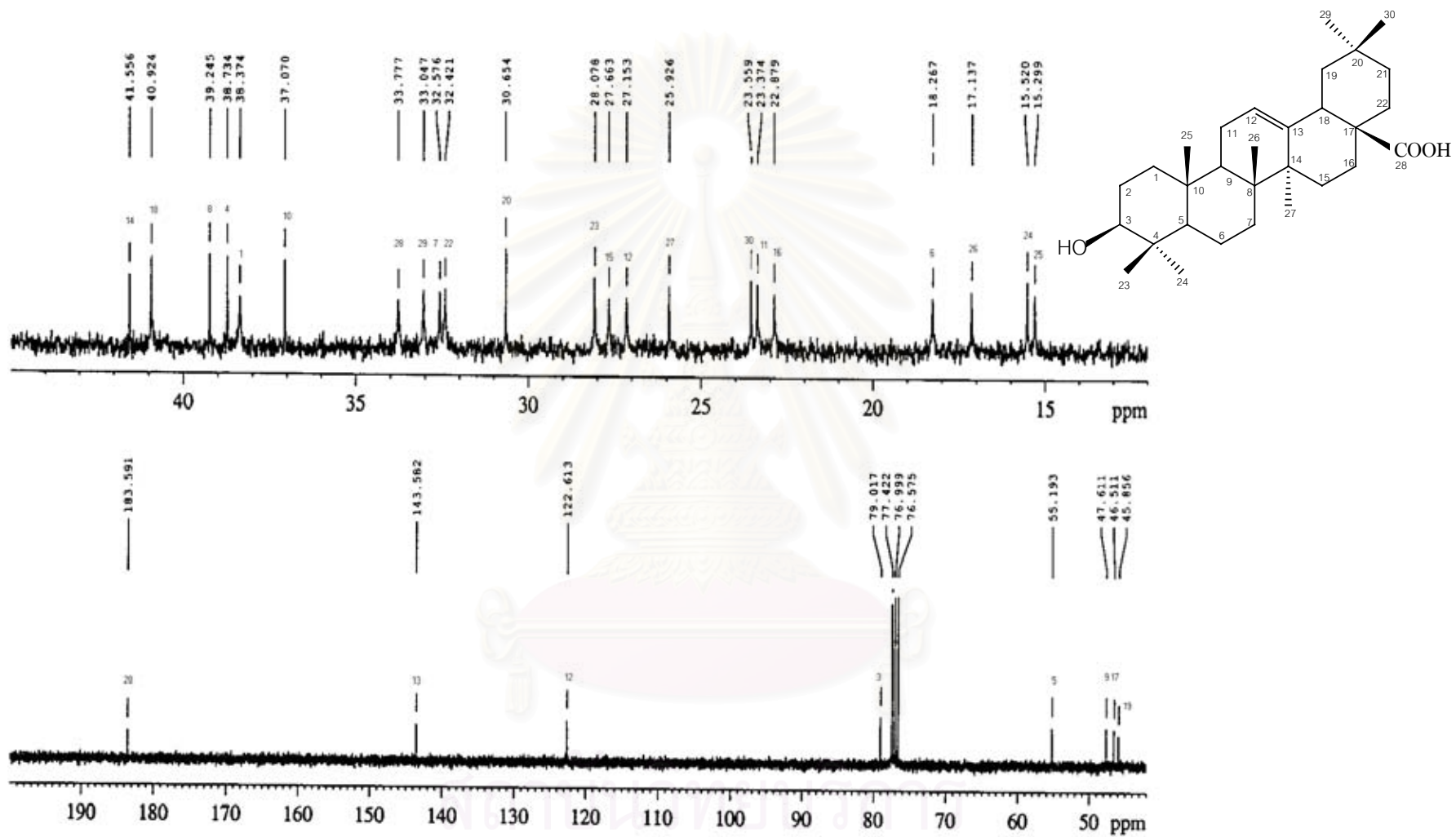


Figure 39b. The 75 MHz ^{13}C NMR spectrum of compound DG6 (expanded)

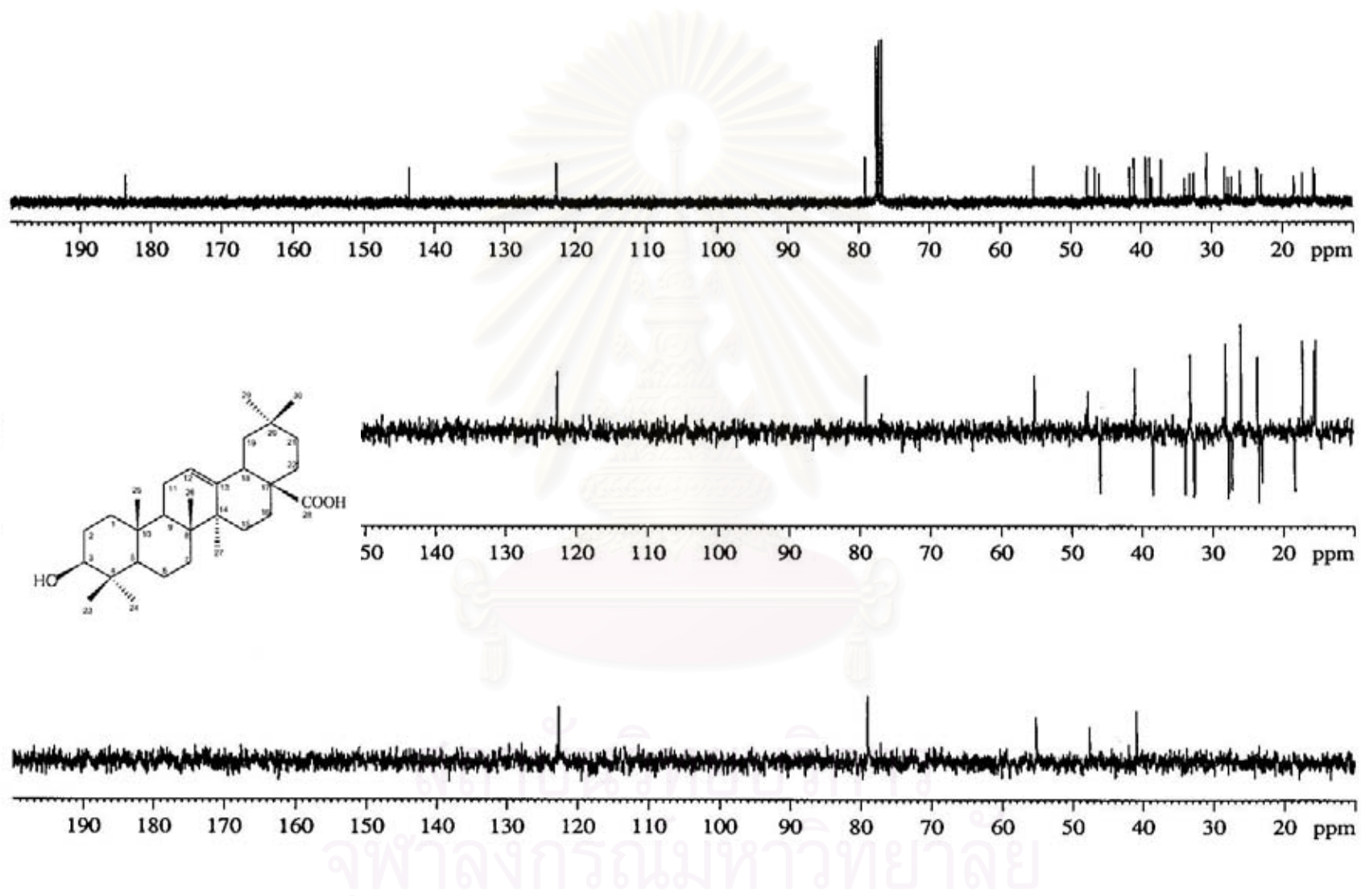


Figure 40a. The 75 MHz ^{13}C -DEPT NMR spectrum of compound DG6 (in CDCl_3)

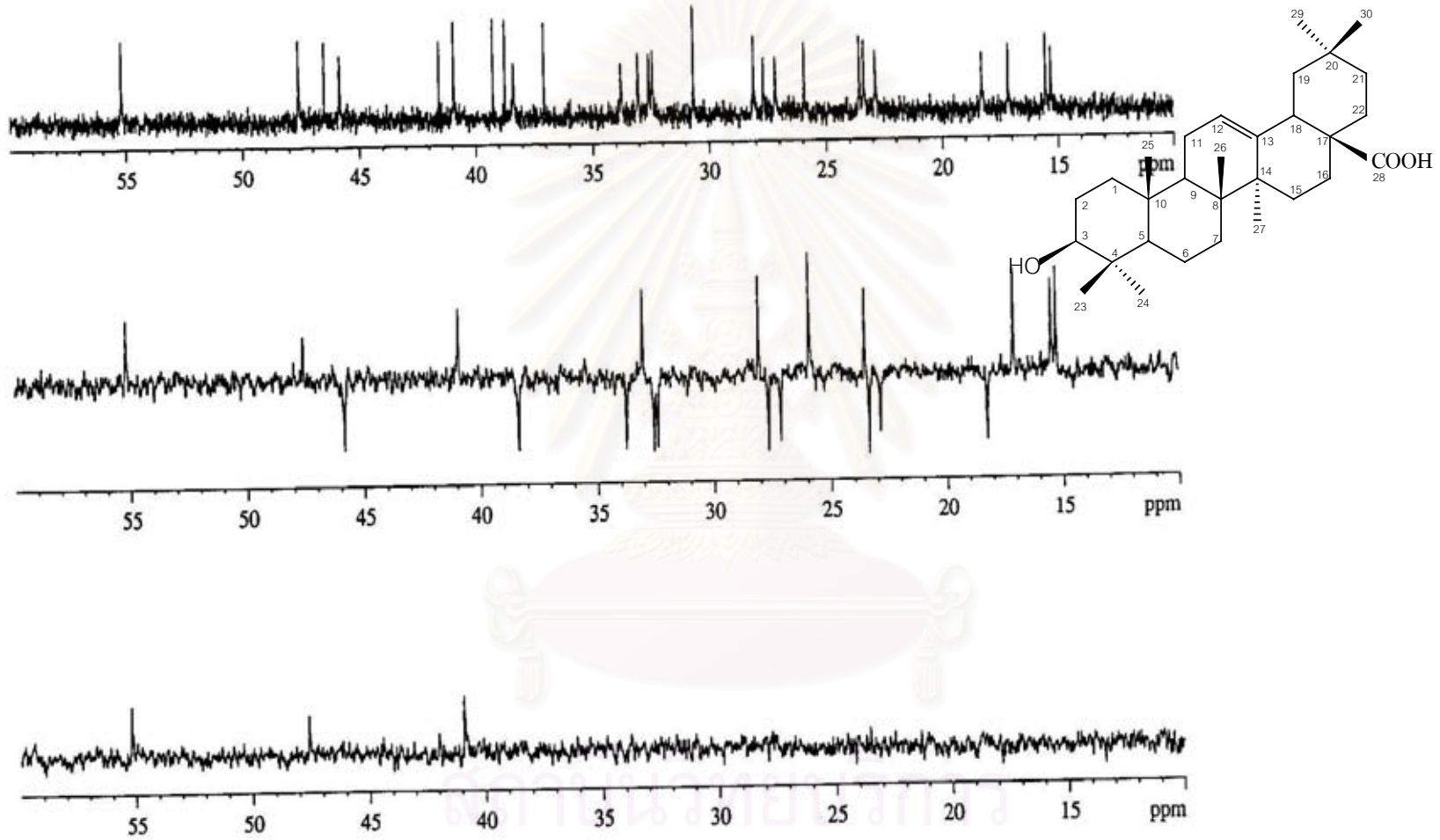


Figure 40b. The 75 MHz ^{13}C -DEPT NMR spectrum of compound DG6 (expanded)

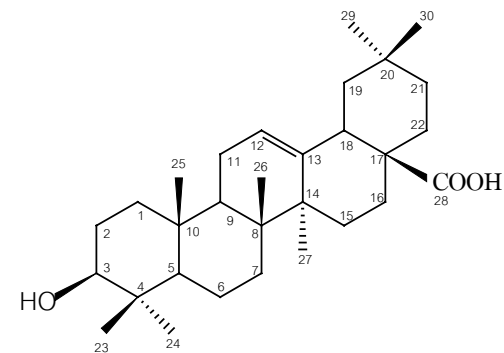
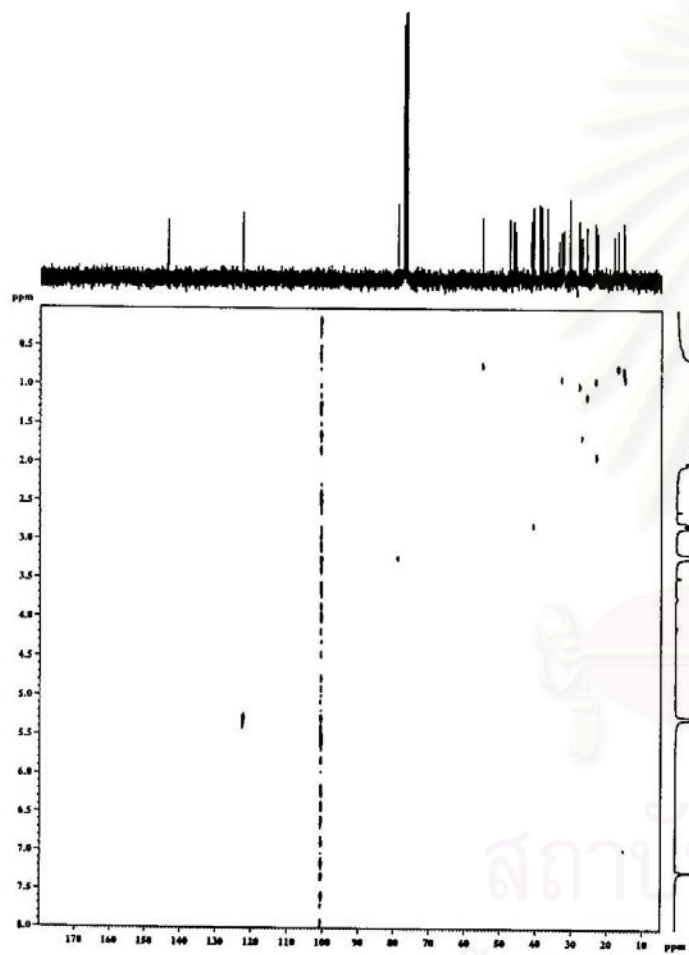


Figure 41a. The 75 MHz ^1H - ^{13}C HETCOR NMR spectrum of compound DG6 (in CDCl_3)

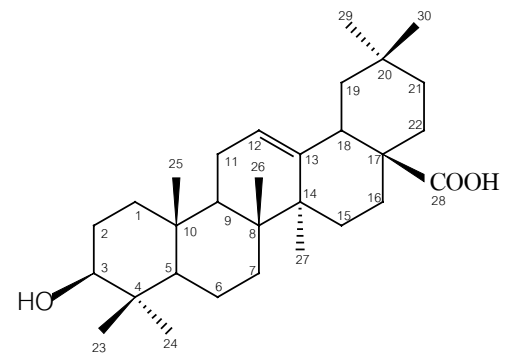
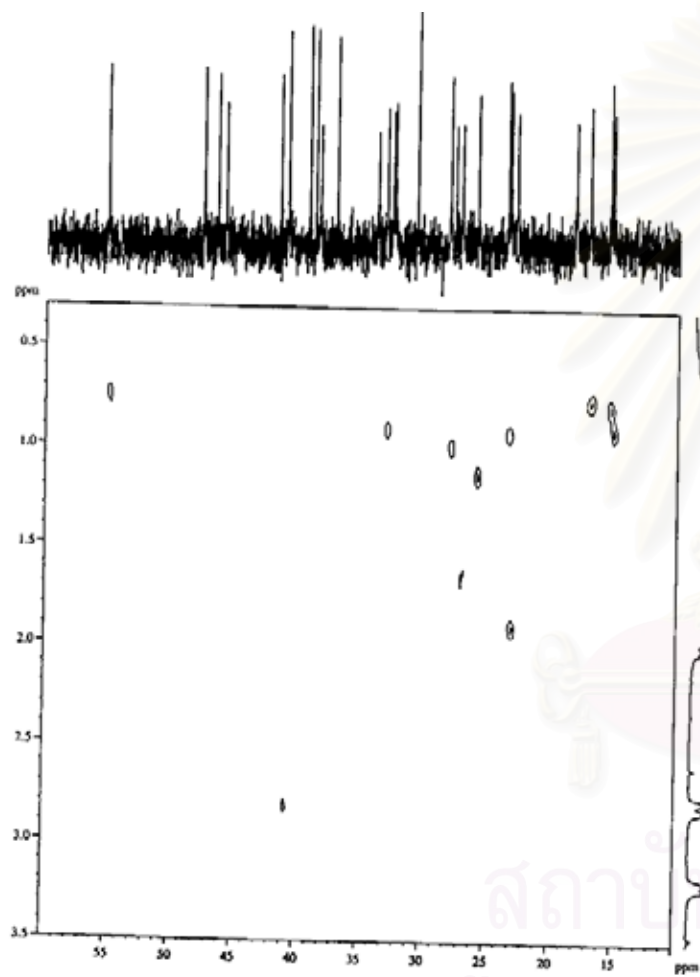


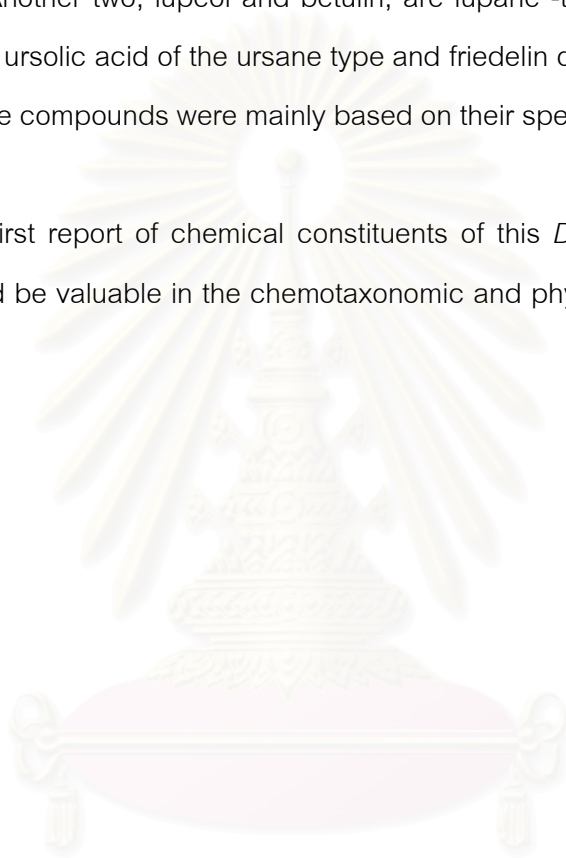
Figure 41b. The 75 MHz ^1H - ^{13}C HETCOR NMR spectrum of compound DG6 (expanded)

CHAPTER V

CONCLUSION

Totally six triterpenoids were isolated from the stems of *Diospyros glandulosa* Lace by chromatographic techniques. Two of them, β -amyrin and oleanolic acid, are oleanane - type triterpenoid. Another two, lupeol and betulin, are lupane -type triterpenoids. The last two compounds are ursolic acid of the ursane type and friedelin of the friedelane type. The identification of these compounds were mainly based on their spectroscopic data.

This is the first report of chemical constituents of this *Diospyros* species and the data obtained would be valuable in the chemotaxonomic and phytochemical studied of this plant genus.



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