

Steroidal glycosides from *Convallaria majalis* whole plants and Their Cytotoxic Activity

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Supplementary Materials

Fig. 1.2. ^1H and ^{13}C NMR spectral for **4**

Fig. 3.4 HMBC and MS spectrometry for **4**

Fig. 5.6. ^1H and ^{13}C NMR spectral for **5**

Fig. 7.8 HMBC and MS spectrometry for **5**

Fig. 9.10. ^1H and ^{13}C NMR spectral for **6**

Fig. 11.12 HMBC and MS spectrometry for **6**

Fig. 13.14. ^1H and ^{13}C NMR spectral for **10**

Fig. 15.16 HMBC and MS spectrometry for **10**

Fig. 17.18. ^1H and ^{13}C NMR spectral for **11**

Fig. 19.20 HMBC and MS spectrometry for **11**

Fig. 21.22. ^1H and ^{13}C NMR spectral for **12**

Fig. 23.24 HMBC and MS spectrometry for **12**

Fig. 25.26. ^1H and ^{13}C NMR spectral for **13**

Fig. 27.28 HMBC and MS spectrometry for **13**

Fig. 29.30. ^1H and ^{13}C NMR spectral for **13a**

Fig. 31.32 HMBC and MS spectrometry for **13a**

Fig. 33.34. ^1H and ^{13}C NMR spectral for **14**

Fig. 35.36 HMBC and MS spectrometry for **14**

Fig. 37.38. ^1H and ^{13}C NMR spectral for **15**

Fig. 39.40 HMBC and MS spectrometry for **15**

Fig.41. Toxicity curves of **1** and **8**.

Chemical shift (ppm) labels above the spectrum: 8.3984, 8.3118, 7.7781, 7.5746, 7.3178, 7.2091, 7.0466, 7.0008, 6.9191, 6.8177, 6.7401, 6.5882, 6.6044, 6.5006, 6.4232, 6.2532, 6.2457, 6.1818, 6.1544, 6.1095, 6.0747, 6.0204, 5.9470, 5.8430, 5.7925, 5.5025, 4.8264, 4.7125, 4.7412, 4.6938, 4.1368, 4.0938, 3.8237, 3.8135, 3.7131, 3.6938, 3.4420, 3.4232, 2.7403, 2.7374, 2.7174, 2.6600, 2.6435, 2.5925, 2.1382, 2.0938, 2.0540, 2.0400, 1.8510, 1.8444, 1.5144, 1.4942, 1.3819, 1.3604, 1.3144, 1.2991, 1.2863, 1.2711, 1.0710, 1.0716, 1.0675, 0.8923, 0.8166.

Integration values below the baseline: 12.843, 0.507, 0.432, 3.984, 0.295, 11.524, 2.030, 1.255, 0.515, 1.000, 0.780, 3.183, 1.279, 1.175, 0.832, 1.784, 1.615, 2.051, 2.051, 2.051, 2.051, 3.940, 1.799, 2.981, 2.981, 4.115, 11.620, 5.553, 3.553, 3.933, 3.933, 1.123, 3.989, 2.560, 2.544, 1.820, 2.427, 3.073, 1.213, 0.711, 3.353, 3.353, 1.749, 1.054, 1.355, 3.189, 3.189, 2.244, 2.251.

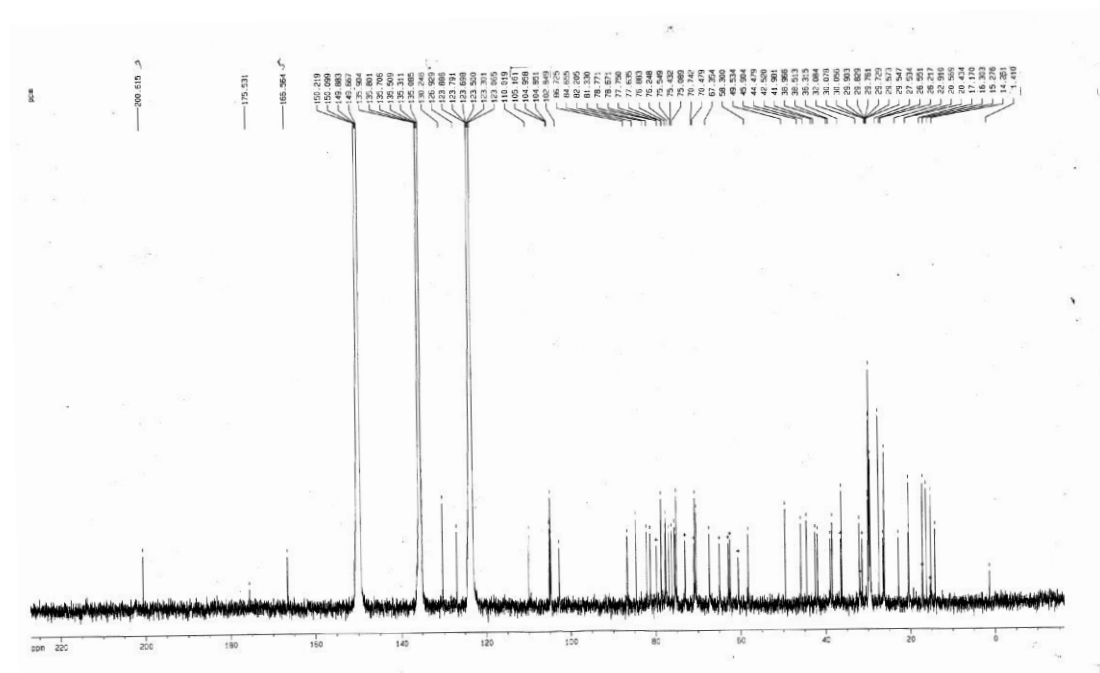
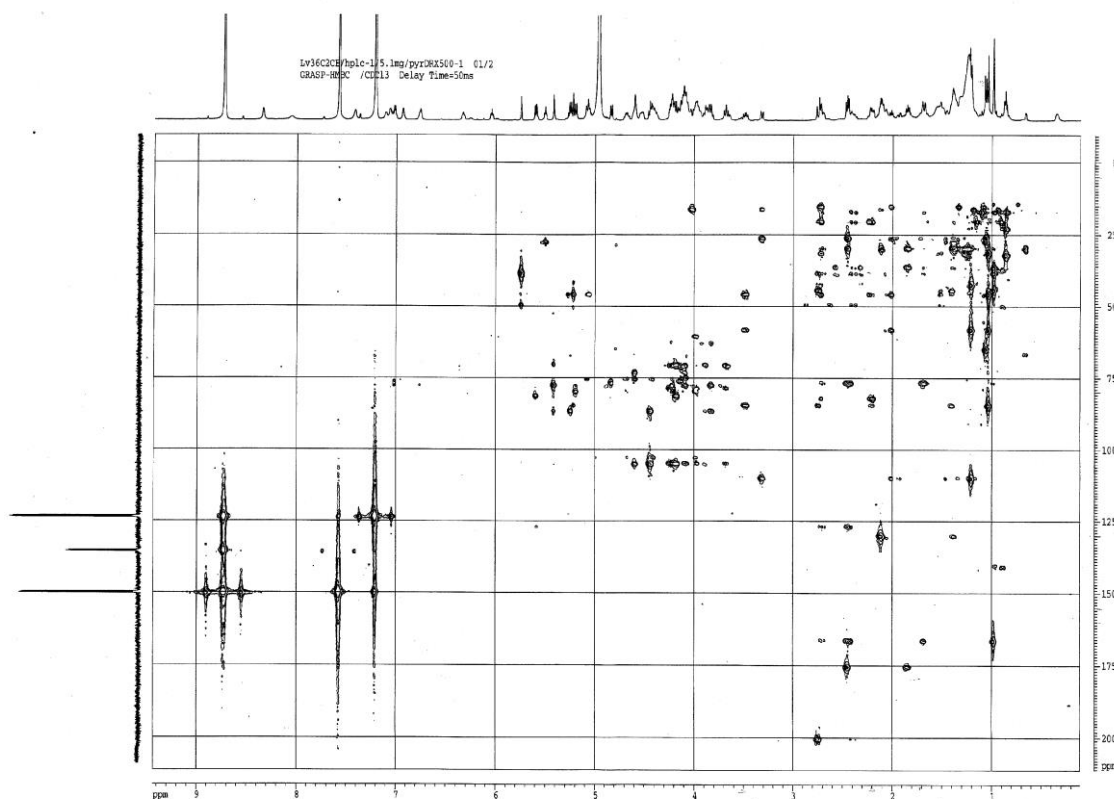


Fig. 3.4. HMBC and MS spectrometry for 4



Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 60.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

17 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

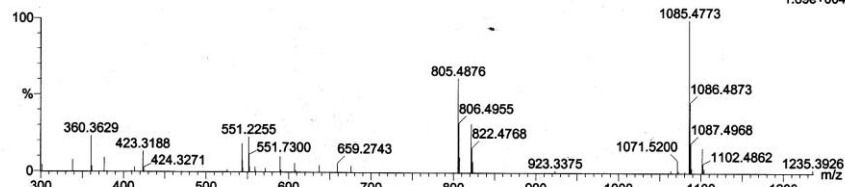
Elements Used:

C: 20-80 H: 30-80 O: 23-24 Na: 0-1

LV36C2CEH1

SHINODA 001 104 (1.964) AM (Cen,4, 80.00, Ar,0.0,0.00,0.70); Sm (SG, 1x3.00); Cm (99:107)

TOF MS ES+
1.89e+004



Minimum:
Maximum:

		5.0	10.0	-1.5					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula			
1085.4773	1085.4781	-0.8	-0.7	11.5	179.3	C50 H78 O24 Na			
	1085.4805	-3.2	-2.9	14.5	245.2	C52 H77 O24			

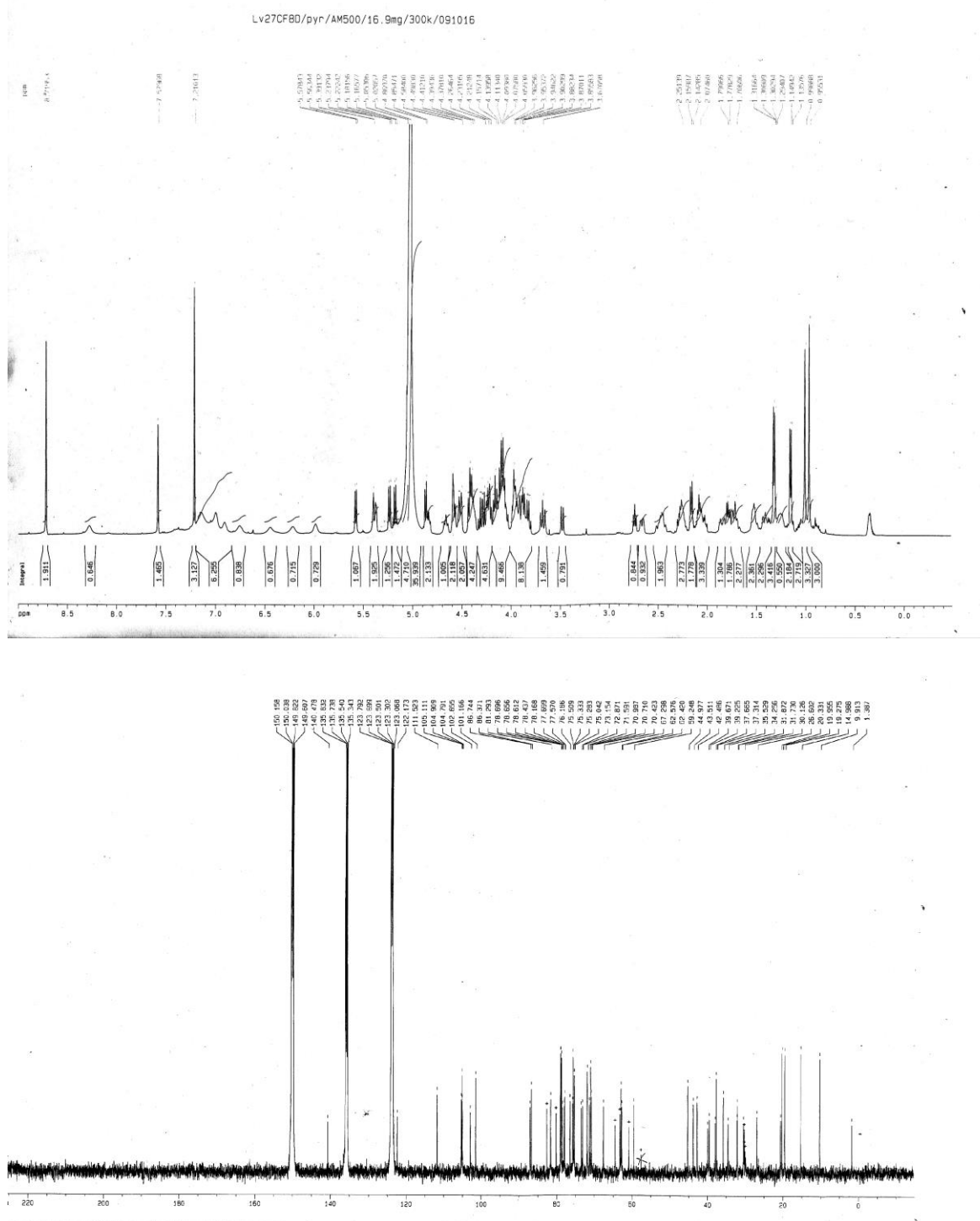
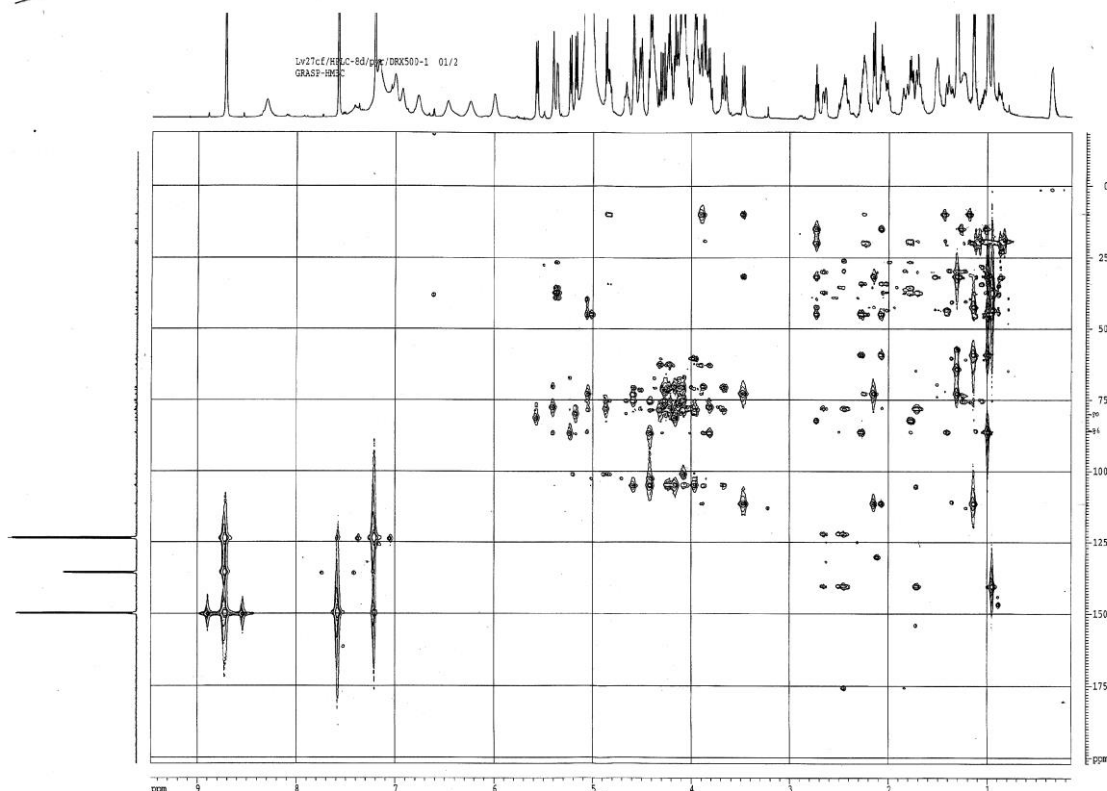


Fig. 7.8. HMBC and MS spectrometry for **5**



Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 60.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

143 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)

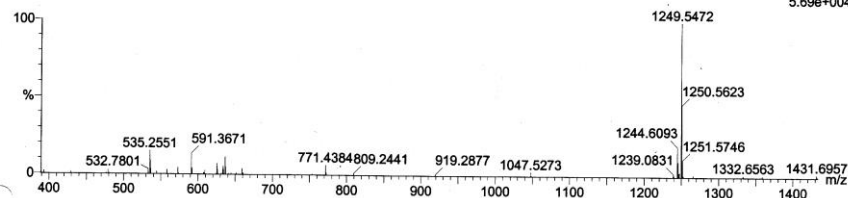
Elements Used:

C: 20-80 H: 30-100 B: 0-1 O: 27-29 Na: 0-1 I: 0-1

LV 27CF8D

SHINODA 001 24 (0.460) AM (Cen,4, 80.00, Ar,0.0,0.00,0.70); Sm (SG, 1x3.00); Cm (21:32)

1: TOF MS ES+
5.69e+004



Minimum:							
Maximum:							
	5.0	10.0	-1.5				
			60.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula	
1249.5472	1249.5465	0.7	0.6	11.5	3993.0	C56	H90 O29 Na
	1249.5461	1.1	0.9	-1.5	1404.3	C47	H99 B O28 I
	1249.5490	-1.8	-1.4	14.5	4548.9	C58	H89 O29
	1249.5450	2.2	1.8	18.5	4046.8	C60	H86 B O27
	1249.5425	4.7	3.8	15.5	3556.8	C58	H87 B O27 Na

Fig. 9.10. ^1H and ^{13}C NMR spectral for **6**

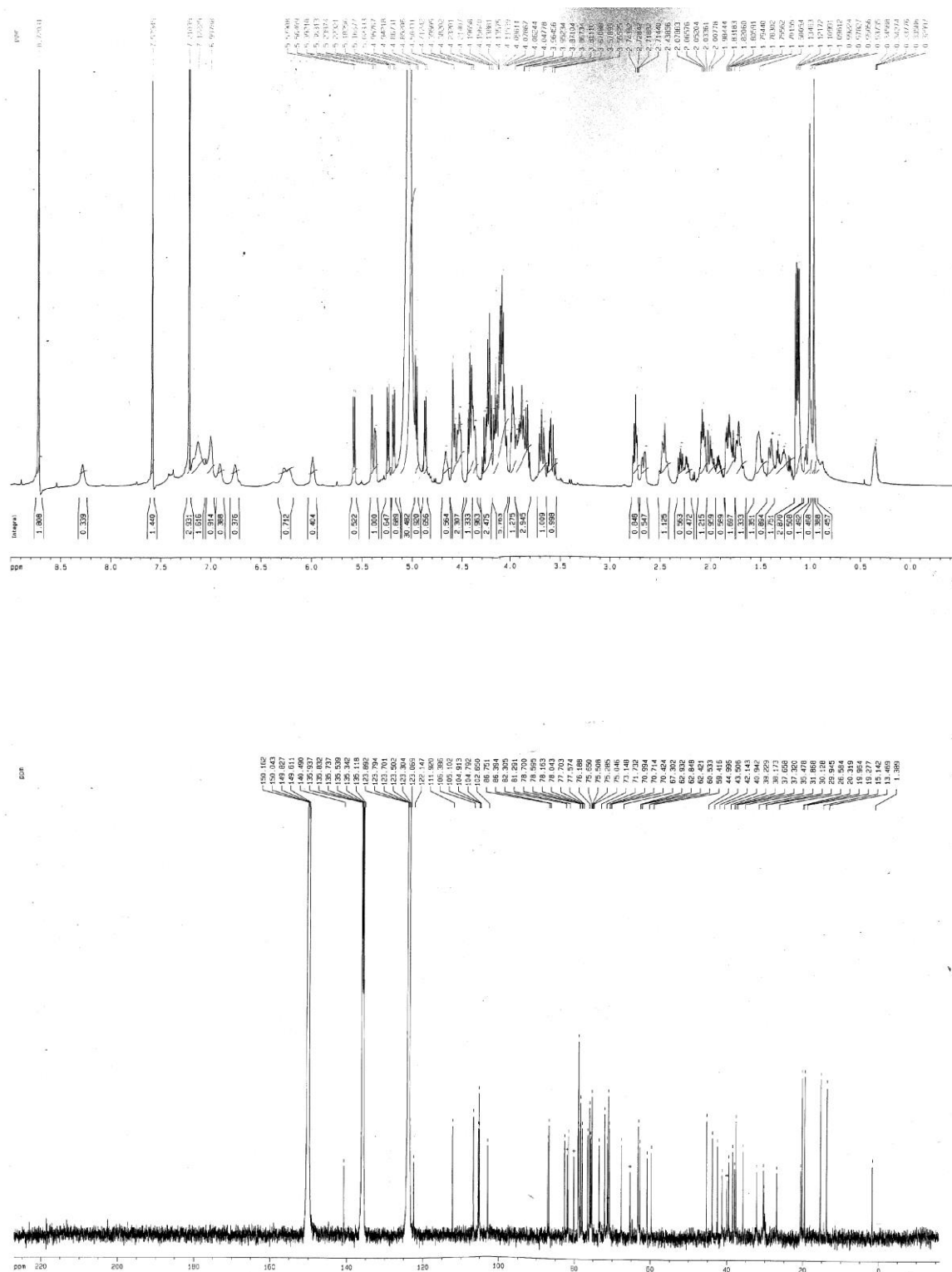
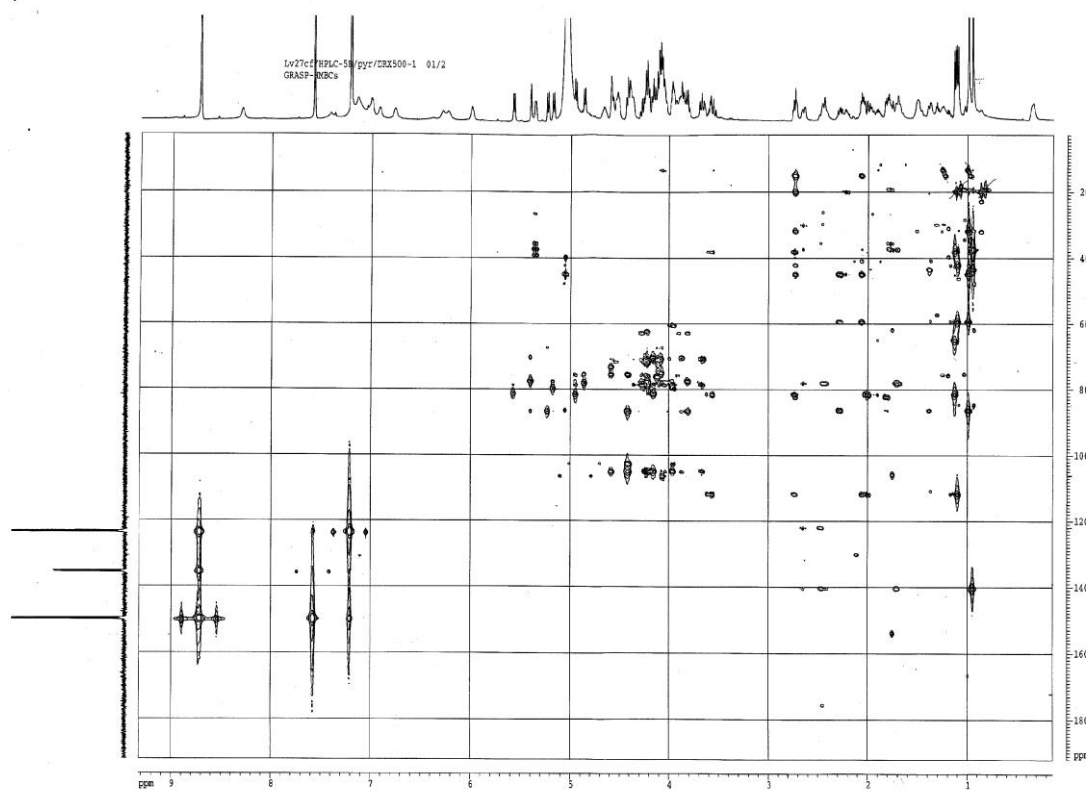


Fig. 11.12. HMBC and MS spectrometry for **6**



Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 40.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

84 formula(e) evaluated with 6 results within limits (all results (up to 1000) for each mass)

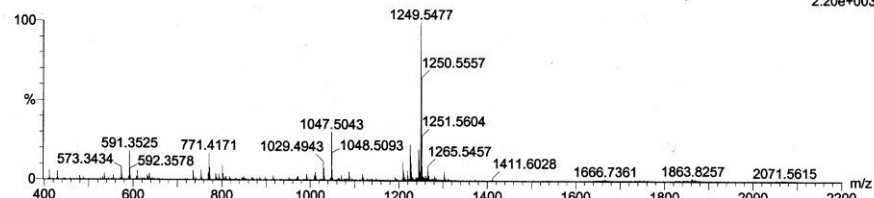
Elements Used:

C: 0-100 H: 0-100 O: 25-29 Na: 0-1

LV 27CF5B2

SHINODA001 72 (1.361) AM (Cen,4, 80.00, Ht,0.0,0.00,0.70); Sm (SG, 1x3.00); Cm (63:72)

1: TOF MS ES+
2.20e+003



Minimum:

Maximum:

		5.0	20.0	-1.5		
				40.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
1249.5477	1249.5490	-1.3	-1.0	14.5	0.5	C58 H89 O29
	1249.5465	1.2	1.0	11.5	1.0	C56 H90 O29 Na
	1249.5618	-14.1	-11.3	15.5	2.7	C60 H90 O26 Na
	1249.5254	22.3	17.8	16.5	5.6	C59 H86 O27 Na
	1249.5642	-16.5	-13.2	18.5	5.7	C62 H89 O26
	1249.5278	19.9	15.9	19.5	6.6	C61 H85 O27

Fig. 13.14. ^1H and ^{13}C NMR spectral for **10**

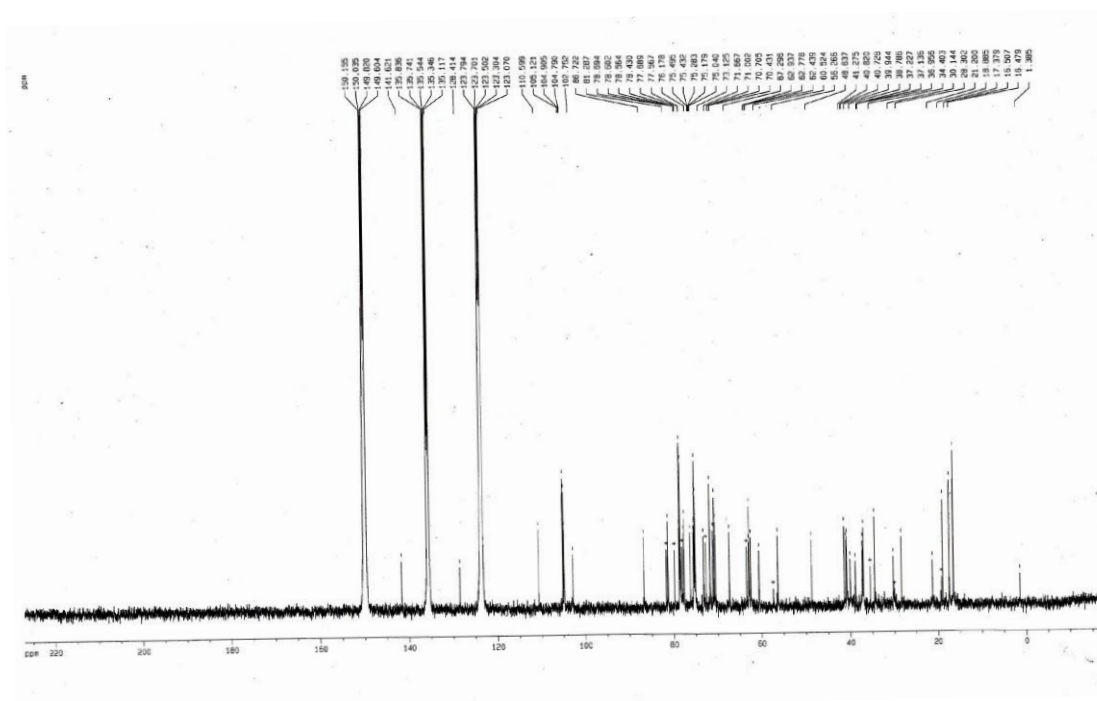
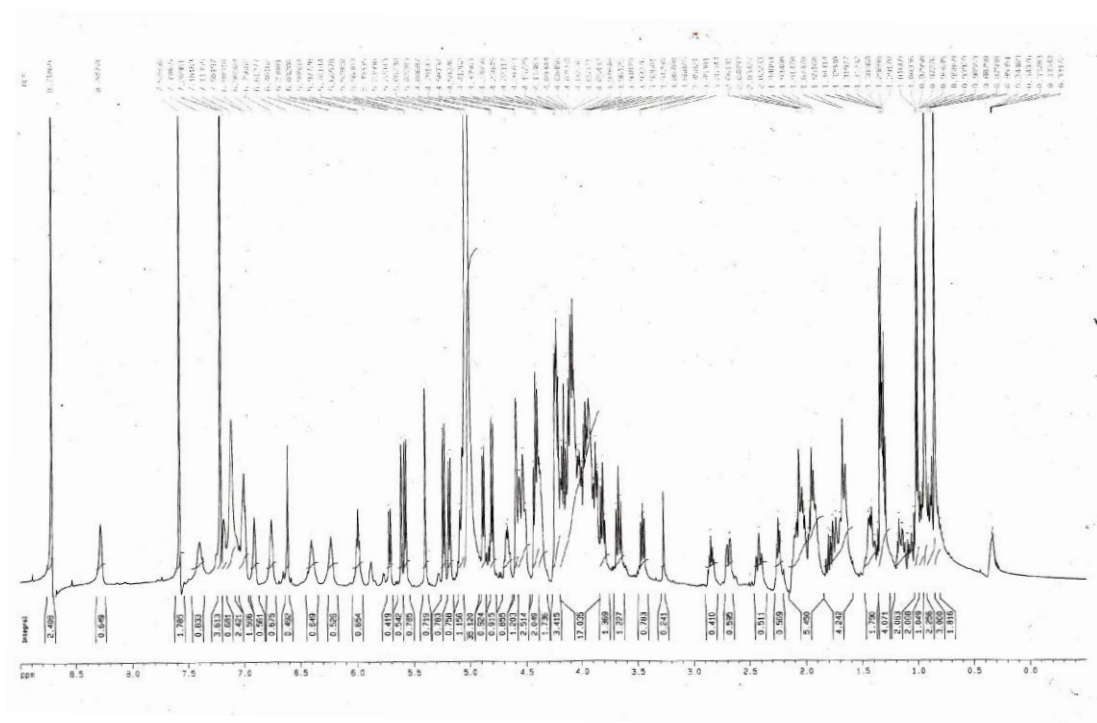
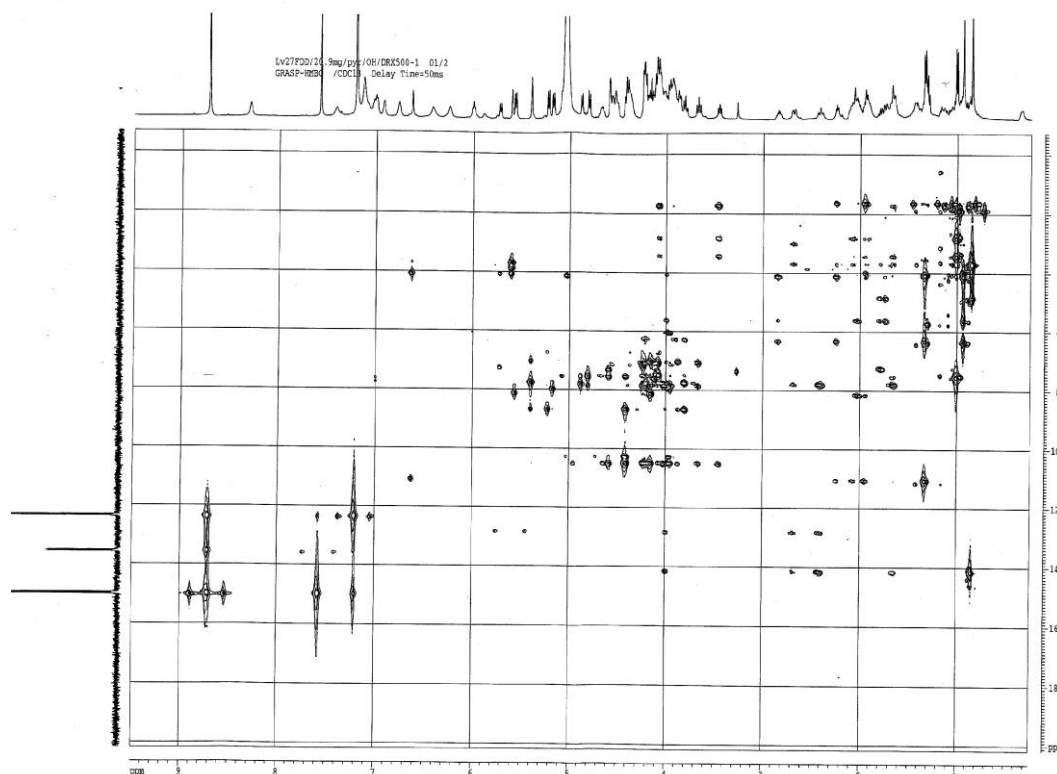


Fig. 15.16. HMBC and MS spectrometry for **10**



Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 300.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

10 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

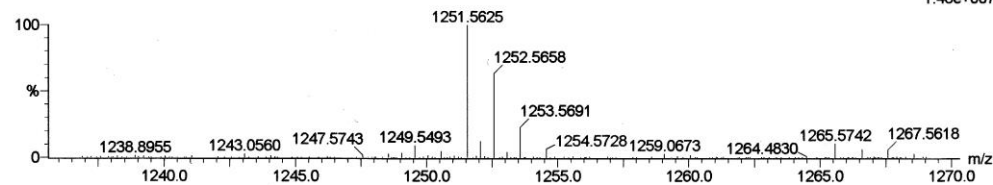
Elements Used:

C: 1-300 H: 1-1000 O: 29-29 Na: 1-1

Lv27FDD2

M-11032 101 (2.115) AM2 (Ar,22000.0,0.00,0.00); ABS; Cm (98:112)

1: TOF MS ES+
1.48e+007



Minimum: -1.5
Maximum: 100.0 20.0 300.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1251.5625	1251.5622	0.3	0.2	10.5	286.1	n/a	n/a	C56 H92 O29 Na

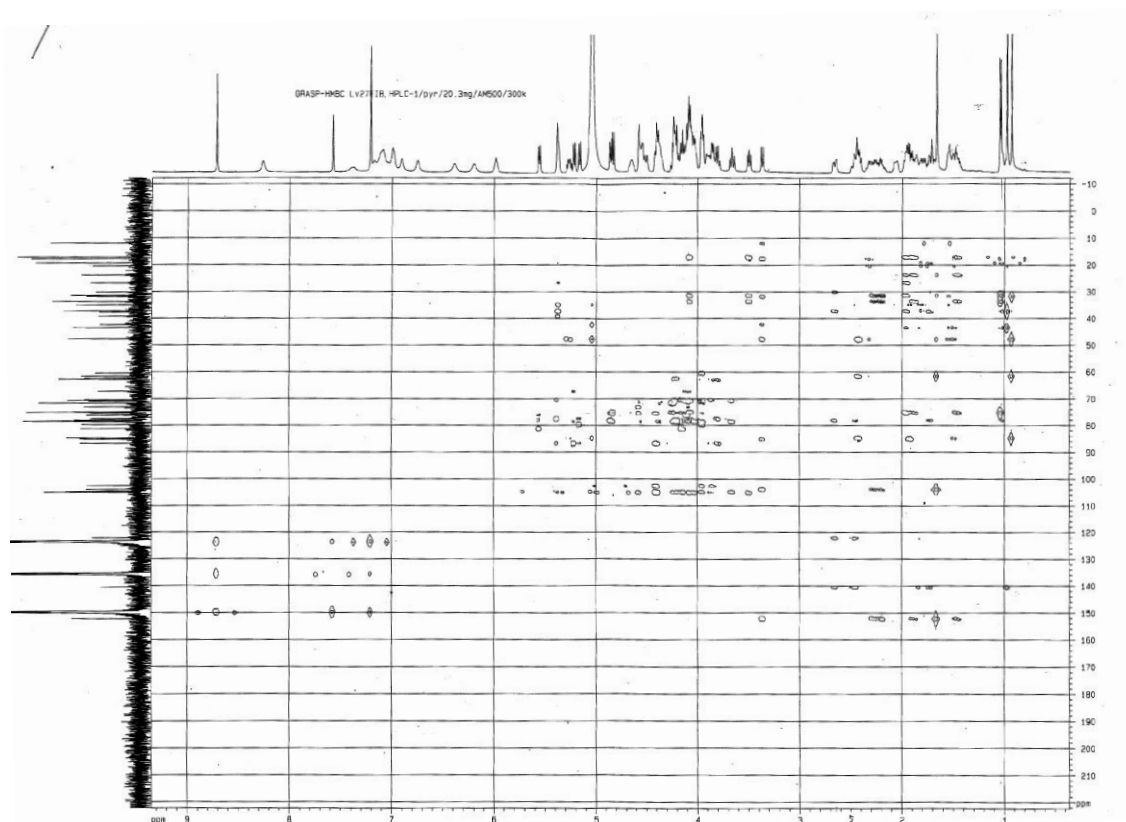
Top Spectrum: ^1H NMR in CDCl_3

Chemical shift range: 0.5 to 8.5 ppm. Integration values are provided below the baseline.

Bottom Spectrum: ^1H NMR in $\text{DMSO}-d_6$

Chemical shift range: 0 to 12 ppm. Integration values are provided below the baseline.

Fig. 19.20 HMBC and MS spectrometry for **11**



Elemental Composition Report

Page 1

Single Mass Analysis (displaying only valid results)

Tolerance = 6.0 PPM / DBE: min = -1.5, max = 40.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

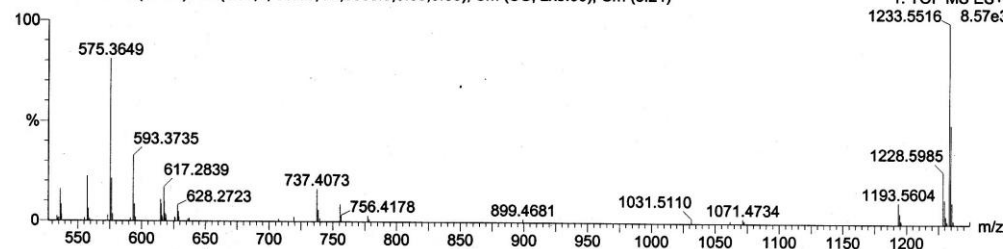
Monoisotopic Mass, Odd and Even Electron Ions

45 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

LV27FIBH11 HPLC-1

SHINODA 002 23 (0.424) AM (Cen,3, 80.00, Ht,5000.0,0.00,0.80); Sm (SG, 2x3.00); Cm (3:24)

23-Oct-2009
1: TOF MS ES+
1233.5516 8.57e3



Minimum: 10.0 6.0 -1.5
Maximum: 40.0

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
1233.5516	1233.5516	0.0	0.0	11.5	1	C56 H90 O28 Na
	1233.5540	-2.4	-1.9	14.5	2	C58 H89 O28

Fig. 21.22. ^1H and ^{13}C NMR spectral for **12**

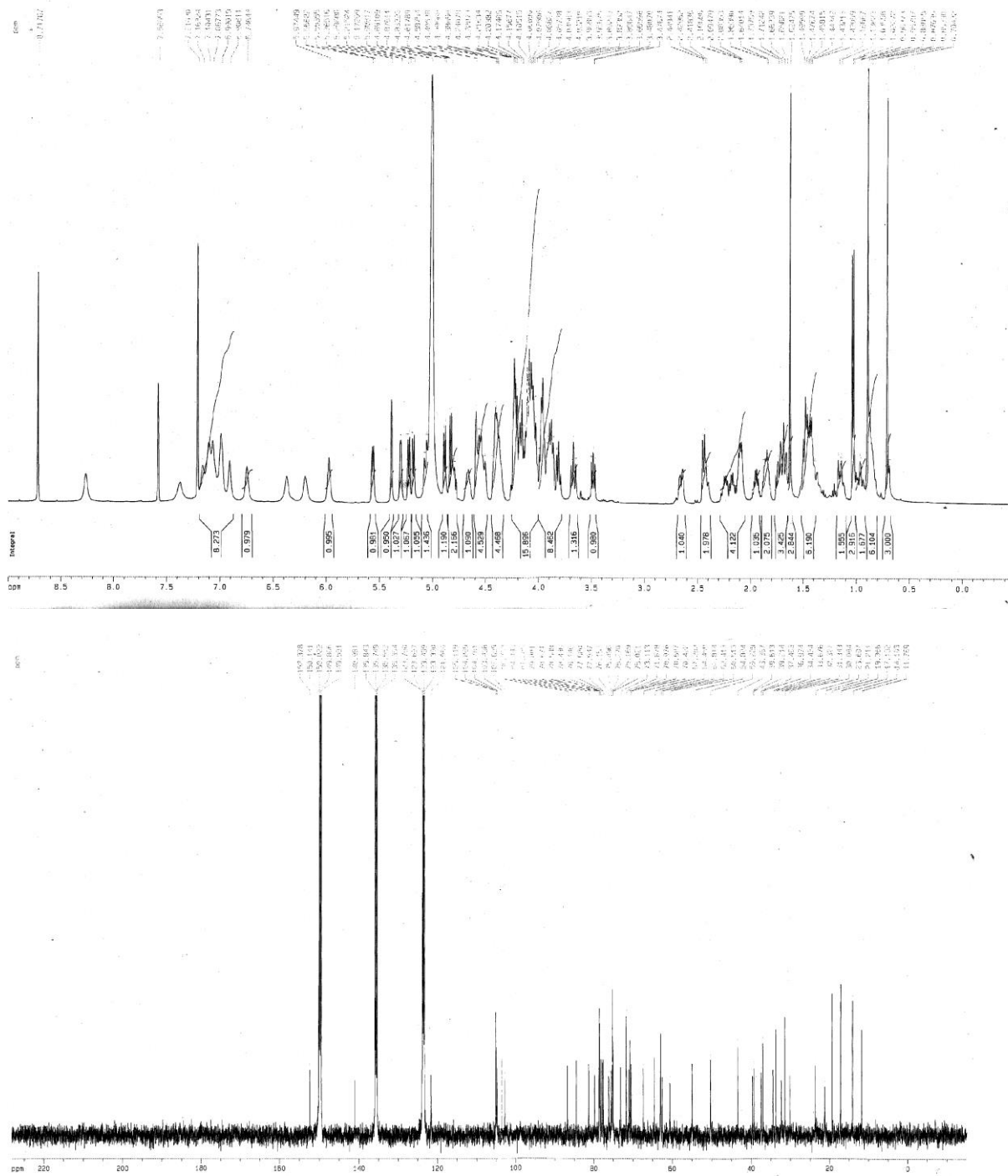
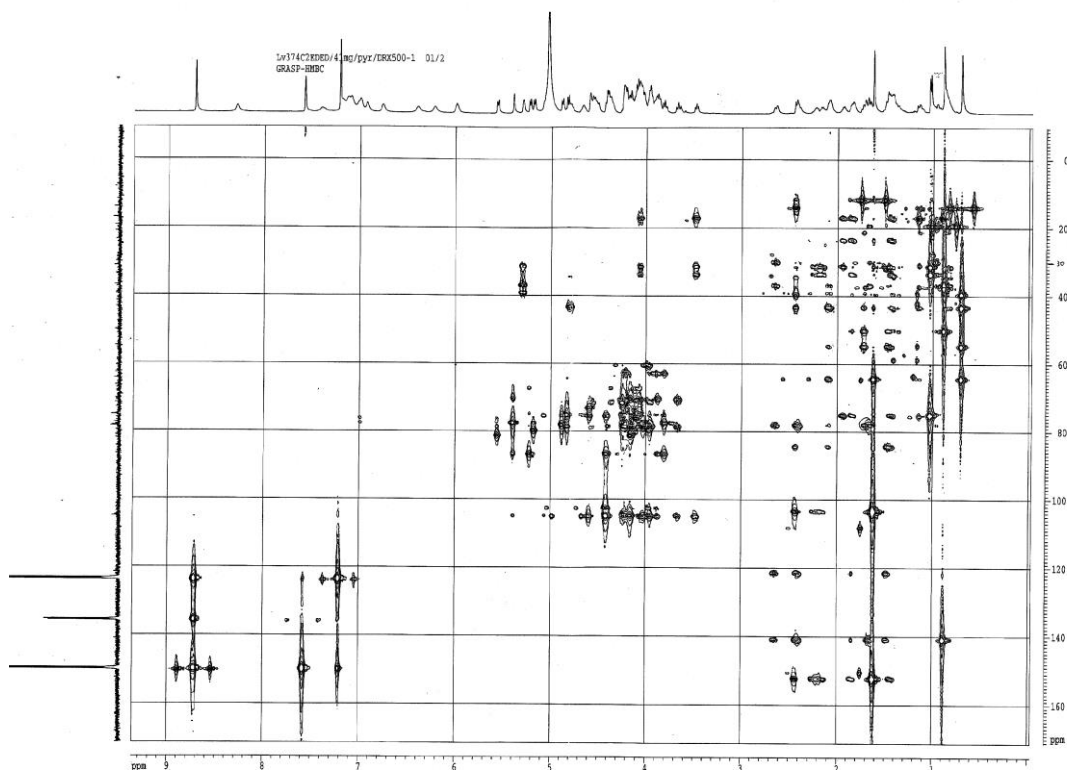


Fig. 23.24. HMBC and MS spectrometry for **12**



Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 300.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

10 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

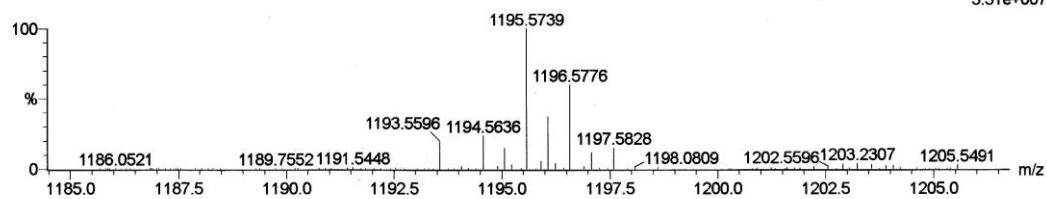
Elements Used:

C: 1-300 H: 1-1000 O: 27-27

Lv374C2ED

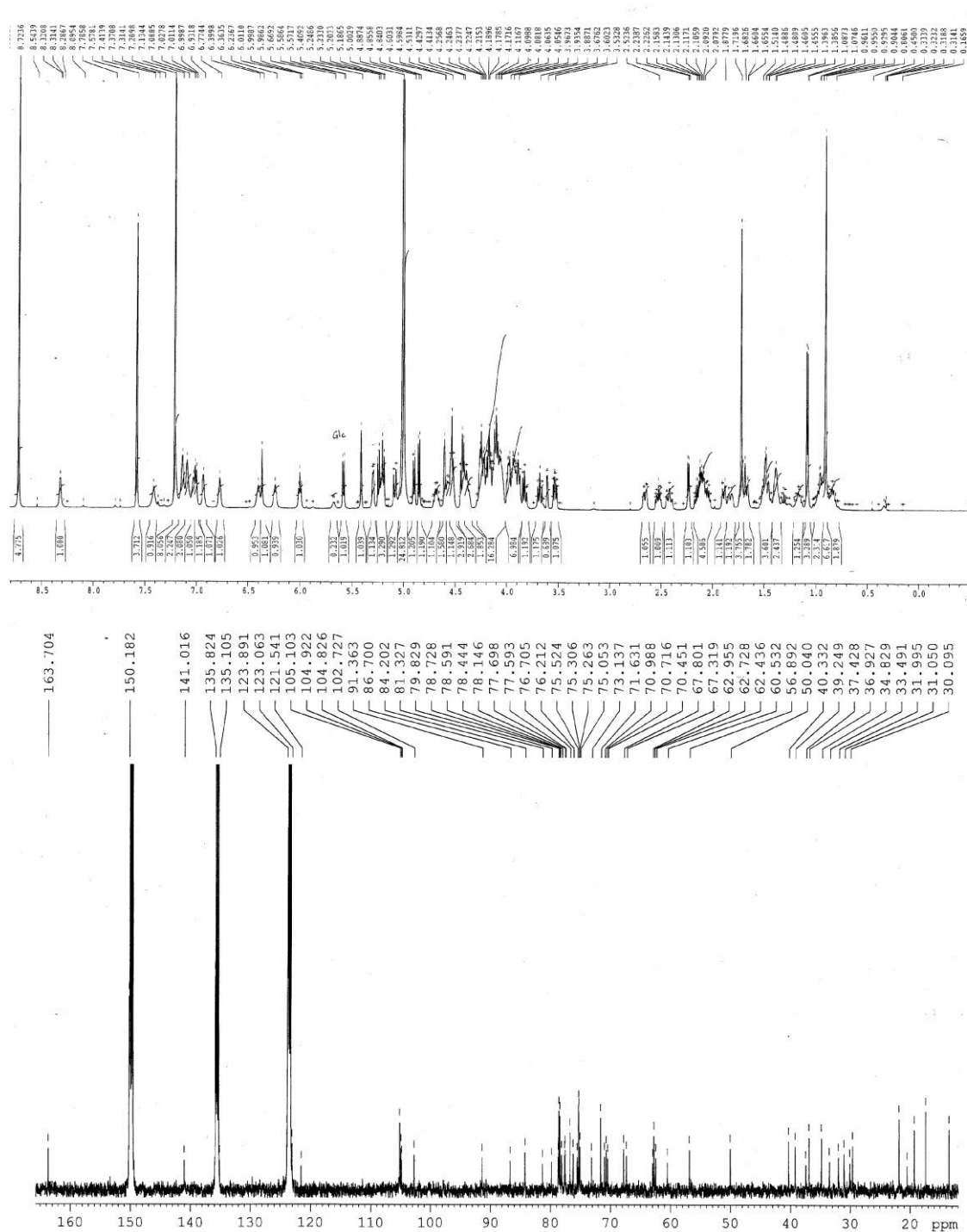
M-11030 167 (3.483) AM2 (Ar,22000.0,0.00,0.00); ABS; Cm (156:170)

1: TOF MS ES+
3.31e+007



Minimum: -1.5
Maximum: 100.0 20.0 300.0

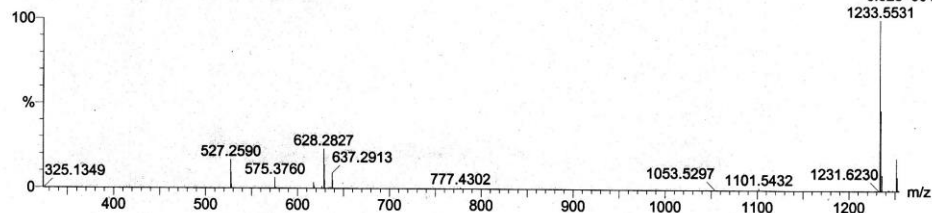
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
1195.5739	1195.5748	-0.9	-0.8	11.5	295.0	n/a	n/a	C56 H91 O27

[illegible]

2D NMR spectrum of compound 1. The x-axis represents chemical shift in ppm (0 to 8), and the y-axis represents chemical shift in ppm (0 to 180). The 1D ^1H NMR spectrum is shown at the top, and the 1D ^{13}C NMR spectrum is shown on the left. The 2D spectrum displays correlations between the two dimensions. A label '1' is present near the bottom center of the 2D plot area.

Page 1

1: TOF MS ES+
6.32e+004
1233.5531



Minimum:				-1.5			
Maximum:		5.0	10.0	60.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula	
1233.5531	1233.5540	-0.9	-0.7	14.5	6476.6	C58 H89	028
	1233.5516	1.5	1.2	11.5	5777.0	C56 H90	028

Fig. 29.30. ^1H and ^{13}C NMR spectral for **13a**

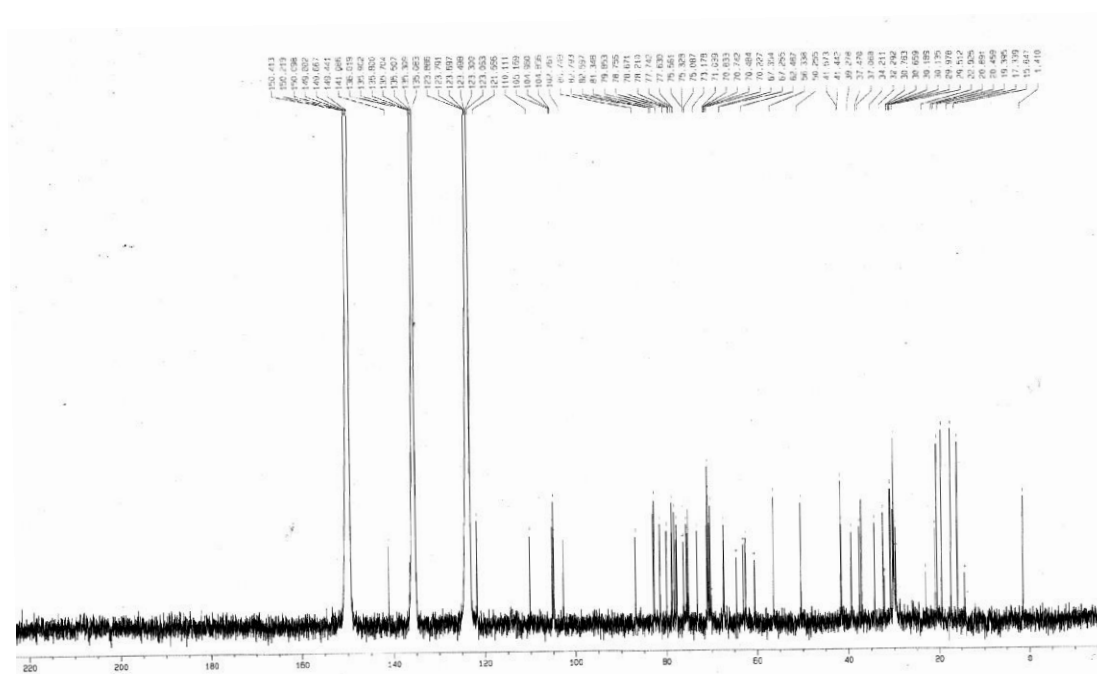
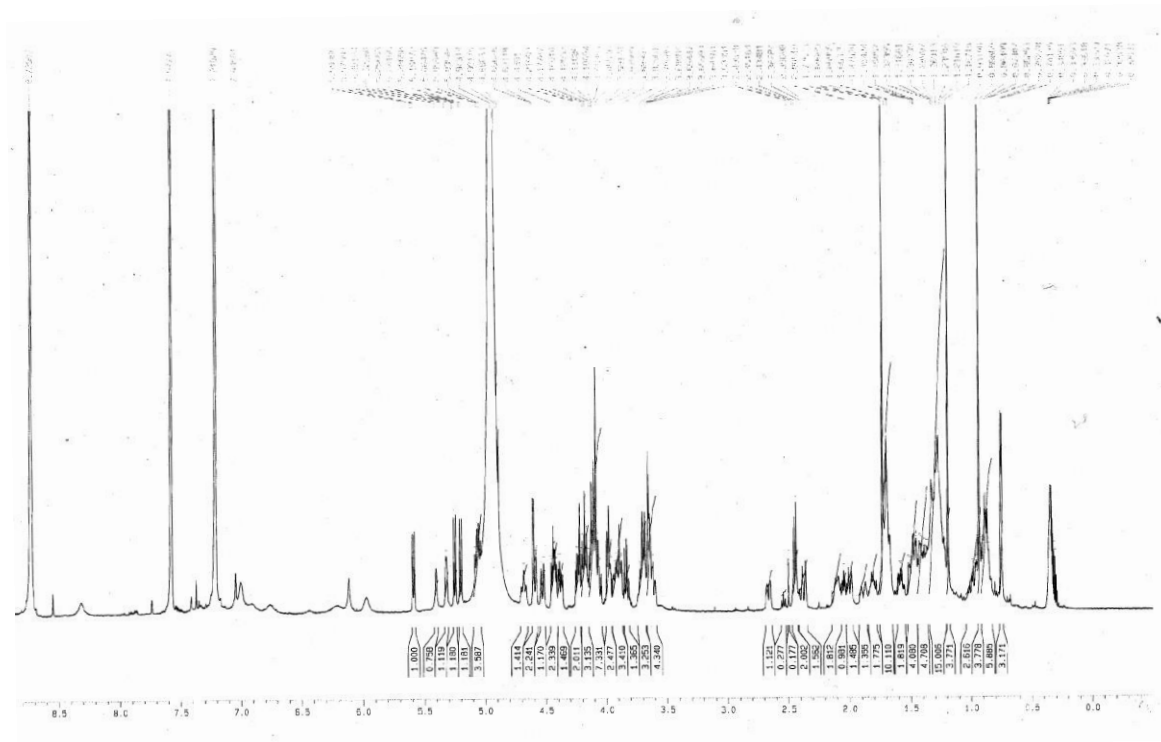
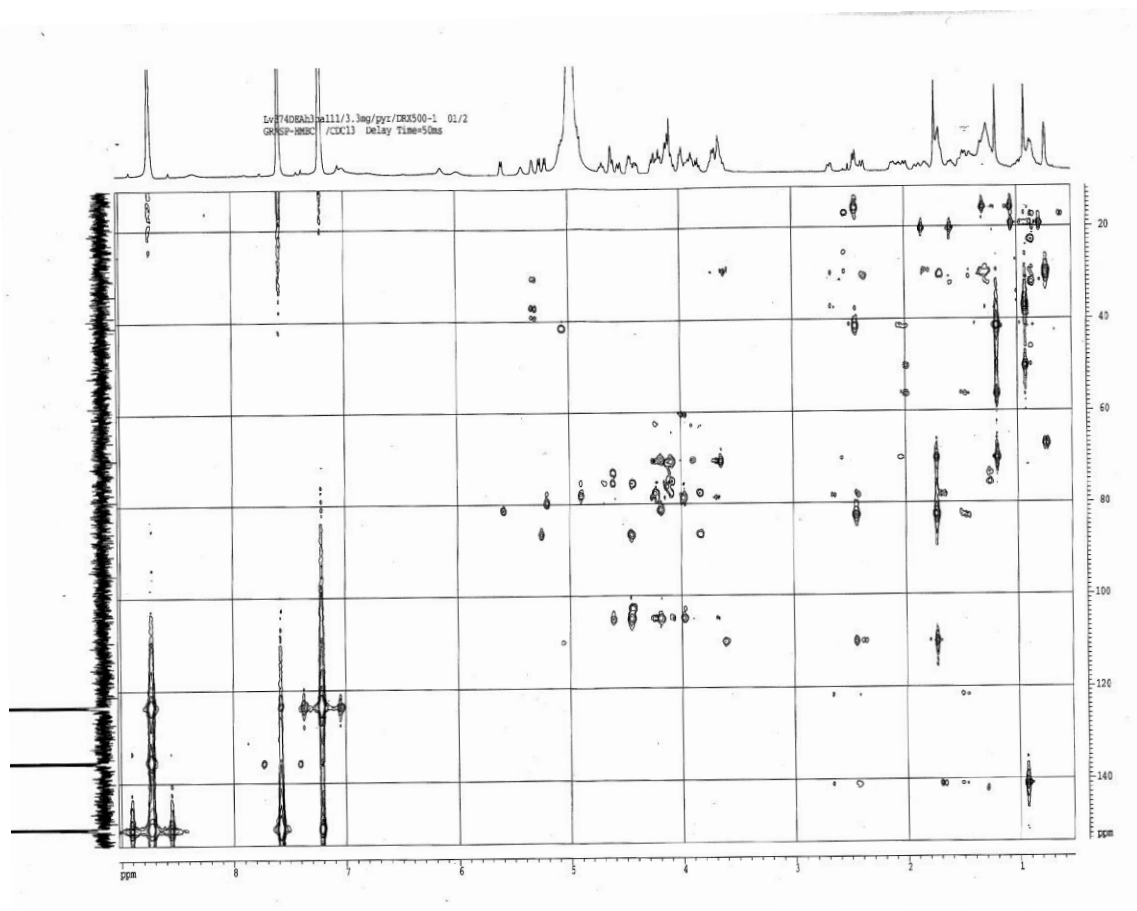


Fig. 31.32 HMBC and MS spectrometry for **13a**



Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 60.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

53 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

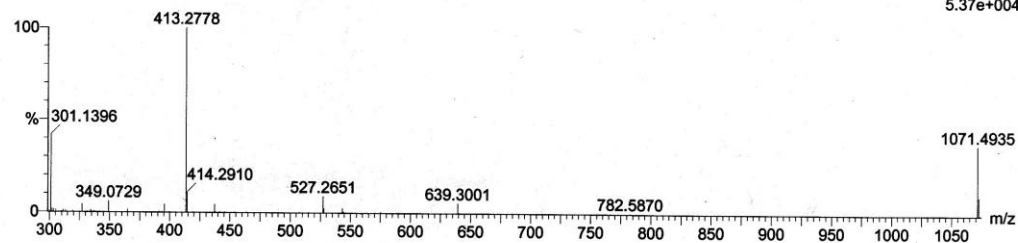
Elements Used:

C: 10-100 H: 10-100 O: 17-23 Na: 1-1

LV374111

SHINODA 001 207 (3.902) AM (Cen,4, 80.00, Ar,0.0,0.00,0.70); Sm (SG, 1x3.00); Cm (207:232)

1: TOF MS ES+
5.37e+004



Minimum:				-1.5			
Maximum:		5.0	15.0	60.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula	
1071.4935	1071.4929	0.6	0.6	19.5	10172.7	C57 H76 O18	Na
	1071.4988	-5.3	-4.9	10.5	9722.1	C50 H80 O23	Na
	1071.4777	15.8	14.7	15.5	9939.4	C53 H76 O21	Na

Fig. 33.34. ^1H and ^{13}C NMR spectral for **14**

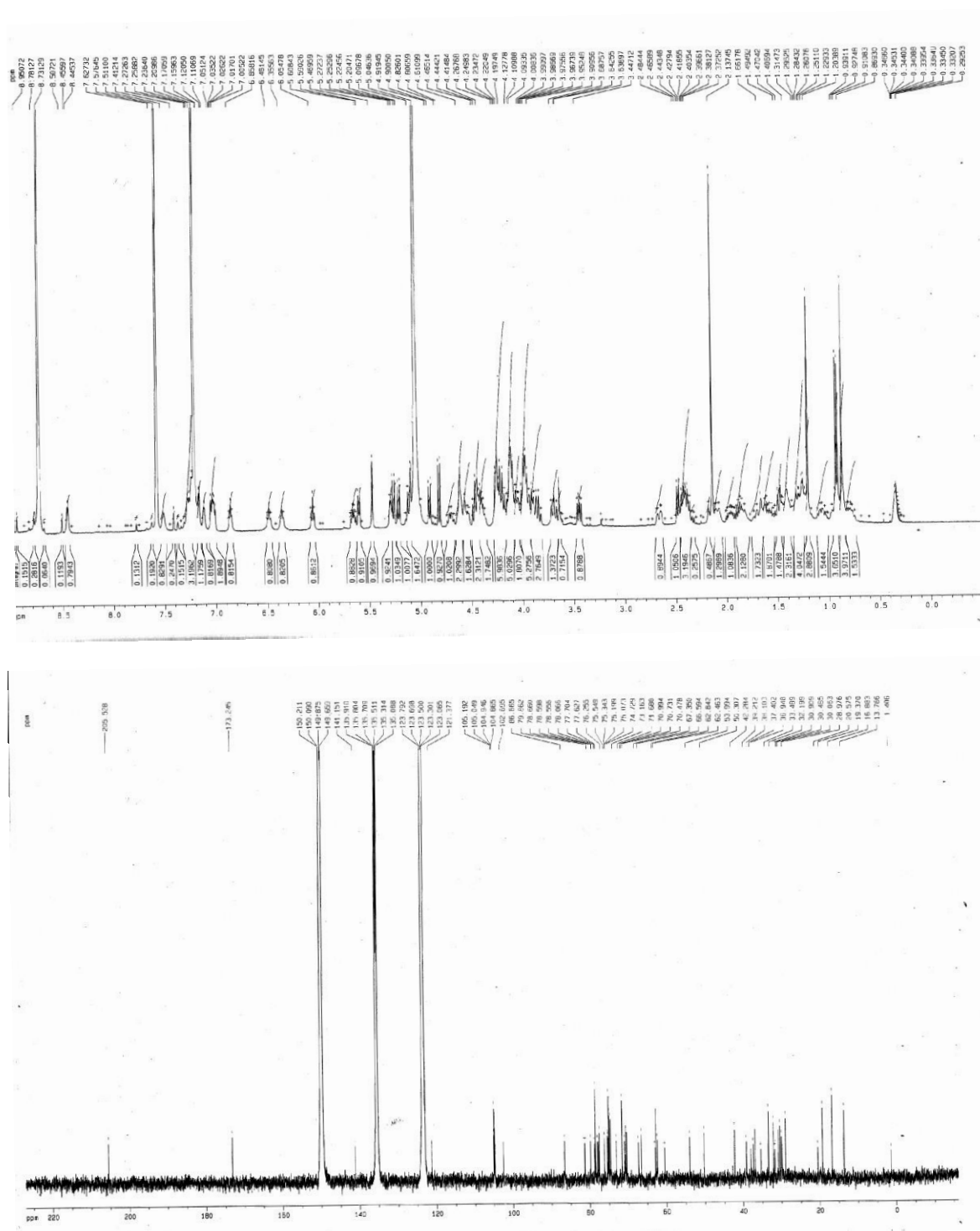
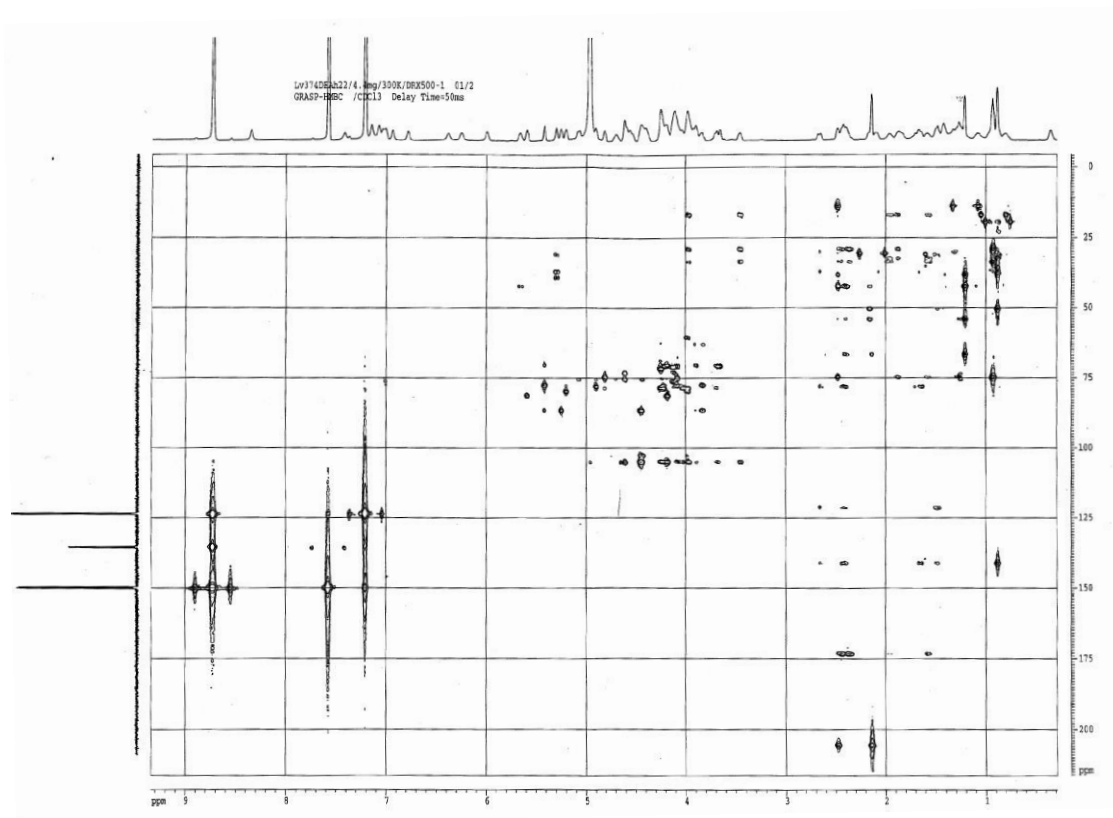


Fig. 35.36. HMBC and MS spectrometry for **14**



Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 300.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

10 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

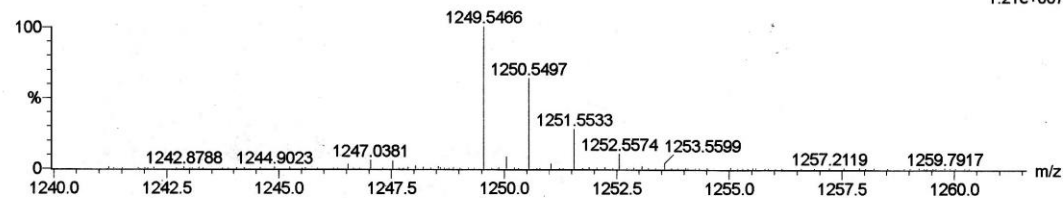
Elements Used:

C: 1-300 H: 1-1000 O: 29-29 Na: 1-1

74DEAH22

M-11031 129 (2.691) AM2 (Ar,22000.0,0.00,0.00); ABS; Cm (115:129)

1: TOF MS ES+
1.21e+007



Minimum: -1.5
Maximum: 300.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
1249.5466	1249.5465	0.1	0.1	11.5	279.7	n/a	n/a	C56 H90 O29 Na

Fig. 37.38. ^1H and ^{13}C NMR spectral for **15**

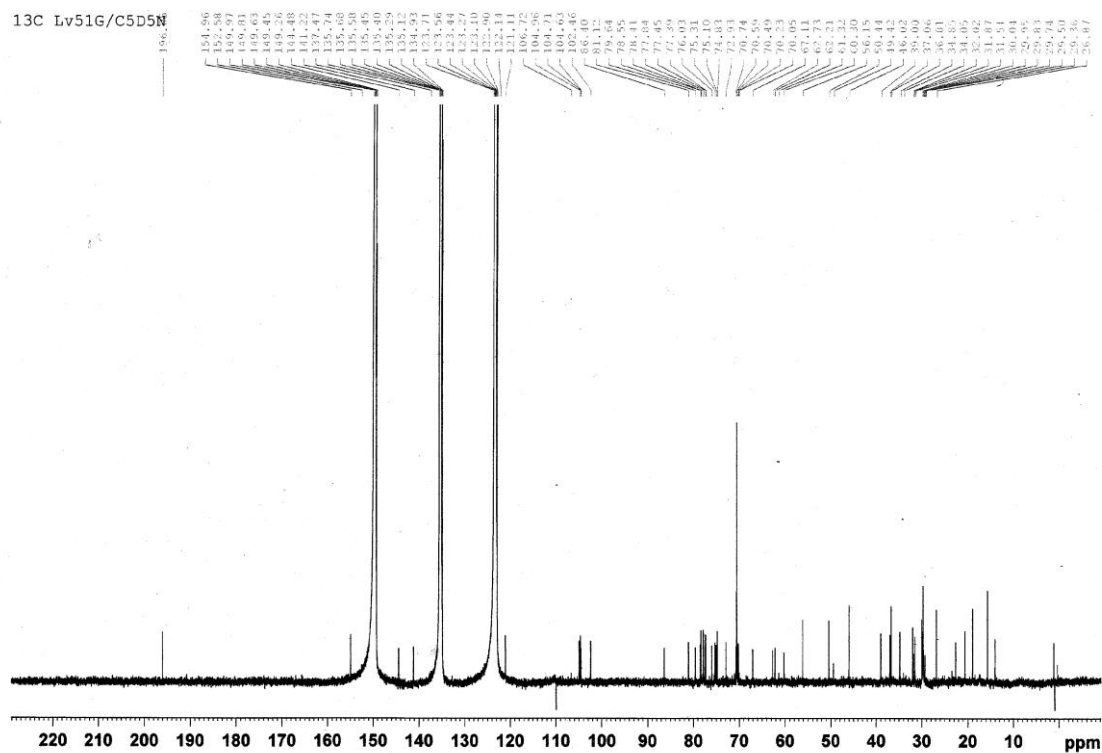
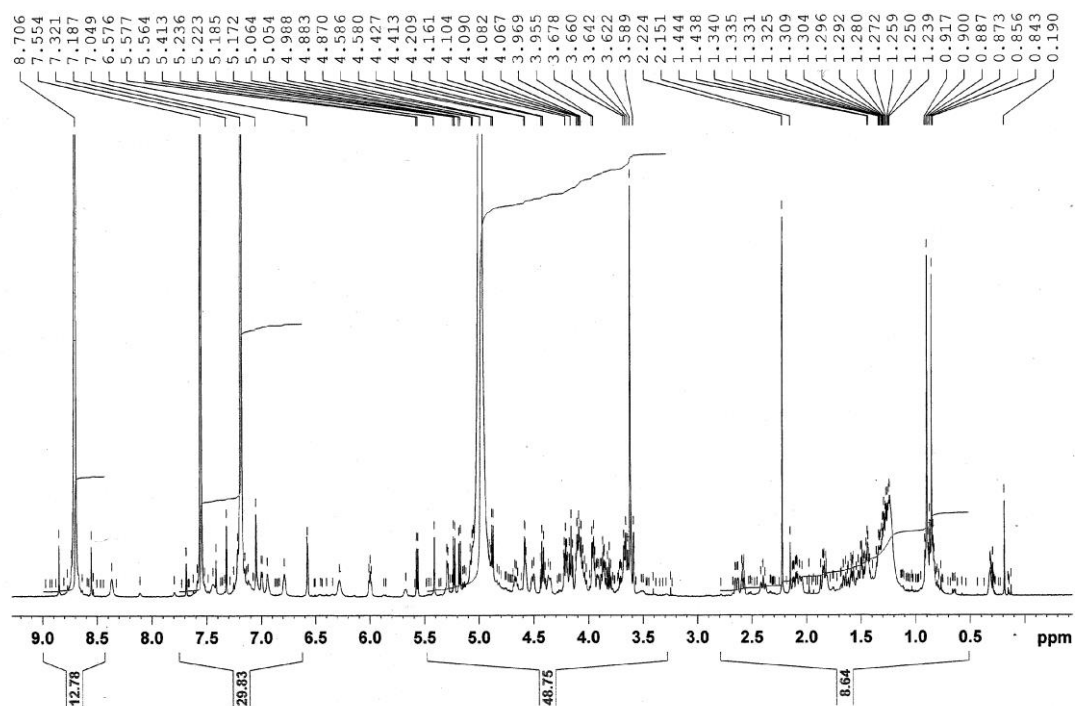
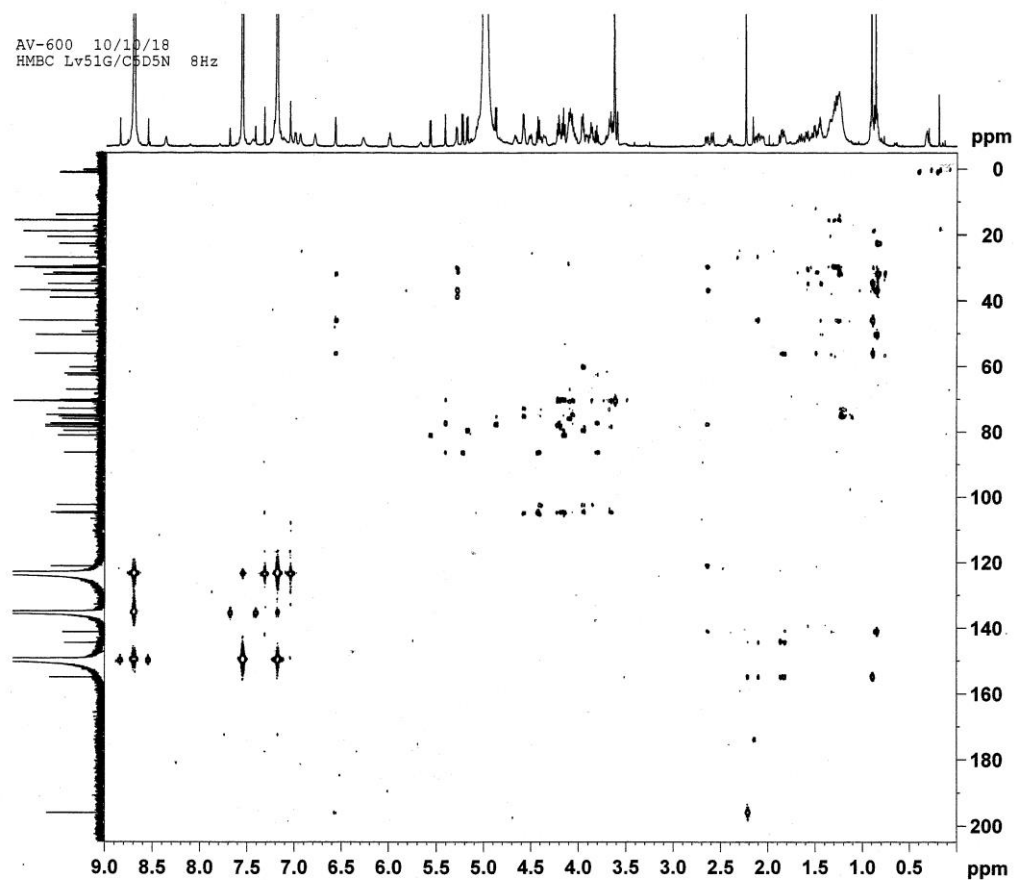


Fig. 39.40 HMBC and MS spectrometry for **15**



Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 60.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

15 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

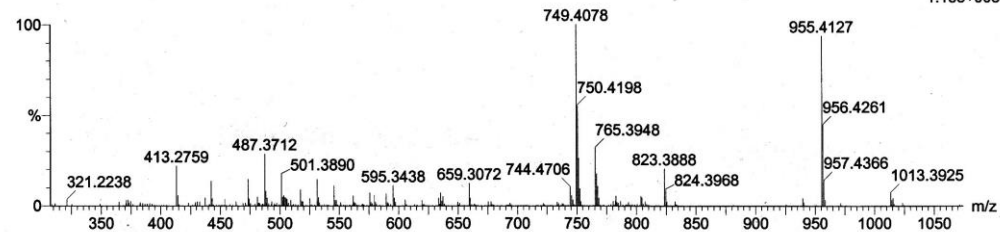
Elements Used:

C: 10-100 H: 10-100 O: 20-21 Na: 1-1

LV51G

SHINODA 001 57 (1.080) AM (Cen,4, 80.00, Ar,0.0,0.00,0.70); Sm (SG, 1x3.00); Cm (54:71)

1: TOF MS ES+
1.13e+005



Minimum: 5.0 15.0 -1.5
Maximum: 60.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
955.4127	955.4151	-2.4	-2.5	10.5	160.2	C44 H68 O21 Na

Fig.41. Toxicity curves of **1** and **8**.

