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Supplementary Information

A total synthesis of Guanacastepene C

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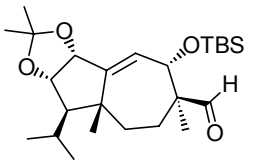
Compound 8:



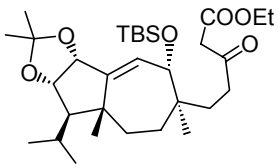
IR (thin film): ν_{max} 2956, 2698, 1728 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.52 (s, 1H), 5.54 (dd, J = 3.9, 1.2 Hz, 1H), 4.94 (d , J = 3.6 Hz, 1H), 4.73 (d, J = 6.3 Hz, 1H), 4.37 (t, *J* = 7.2 Hz, 1H), 1.87-1.54 (m, 5H), 1.50 (s, 3H), 1.35 (s, 3H), 1.30-1.20 (m, 1H),1.14 (s, 3H), 1.05 (d, J = 6.6 Hz, 3H), 0.99 (d, J = 6.6 Hz, 3H), 0.98 (s, 3H), 0.84 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 205.9, 145.9, 111.7, 82.5, 81.0, 52.6, 49.3, 31.8, 28.5, 28.4, 27.1, 26.1, 25.7(2C), 24.4, 21.8, 17.9, -4.2, -5.3.

HRMS (ES) *m/z* calcd for $C_{25}H_{44}NaO_4Si$, $[M+Na]^+$: 459.2907, found : 459.2892

Compound 10:



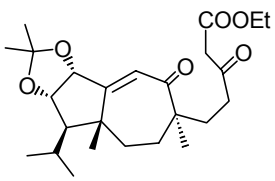
IR (thin film): ν_{max} 2957, 2857, 1746 1719 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.43 (d, J = 3.9 Hz, 1H), 4.69 (d, J = 6.6 Hz, 1H), 4.29 (t, J = 6.9 Hz, 1H), 4.21 (d, J = 4.2 Hz, 1H), 4.13 (q, J = 6.9 Hz, 2H), 3.37 (s, 2H), 2.46-2.40 (m, 2H), 1.75-1.42 (m, 6H), 1.42 (s, 3H), 1.35-1.19 (m, 2H), 1.28 (s, 3H), 1.21 (t, J = 6.9 Hz, 3H), 0.98 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H), 0.87 (s, 3H), 0.82 (s, 9H), 0.74 (s, 3H), -0.03 (s, 3H), -0.04 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 203.1, 167.3, 145.1, 111.7, 82.6, 80.7, 74.4, 61.3, 49.3, 39.8, 38.3, 31.3, 29.7, 28.3, 27.2, 26.2, 25.9, 24.3, 21.9, 18.0, 14.1, 1.0, -4.1, -5.0.

HRMS (ES) *m/z* calcd for $C_{31}H_{54}NaO_6Si$, $[M+Na]^+$: 573.3587, found : 573.3589.

Compound 12:



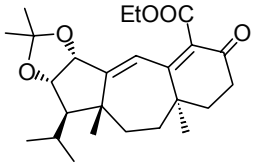
IR (thin film): ν_{max} 2961, 2934, 1744, 1737, 1718 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.93 (d, J = 1.8 Hz, 1H), 4.90 (dd, J = 7.2, 1.5 Hz, 1H), 4.43 (dd, J = 7.5, 6.0 Hz, 1H), 4.19 (q, J = 6.9 Hz, 2H), 3.46 (s, 2H), 2.61-2.54 (m, 2H), 1.92-1.73 (m, 5H), 1.61-1.49 (m, 3H), 1.46 (s, 3H), 1.36 (s, 3H), 1.28 (t, J = 6.9 Hz, 3H), 1.14 (s, 3H), 1.08 (d, J = 6.6 Hz, 3H), 1.04 (s, 3H), 1.03 (d, J = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 207.4, 202.8, 167.3, 161.8, 123.6, 112.7, 82.6, 80.1, 61.4, 60.9, 51.3, 50.1, 49.3, 38.5, 34.3, 32.6, 30.7, 28.0, 27.9, 26.0, 24.7, 23.5, 22.3, 22.2, 14.1.

HRMS (ES) *m/z* calcd for $C_{25}H_{38}NaO_6$, $[M+Na]^+$: 457.2566, found : 457.2577.

Compound 13:



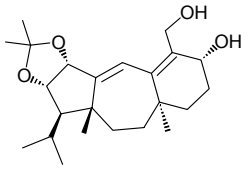
IR (thin film): ν_{max} 2960, 2855, 1735,1671 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.16 (d, J = 2.1 Hz, 1H), 4.87 (d, J = 7.2 Hz, 1H), 4.42 (dd, J = 6.9, 5.7 Hz, 1H), 4.35-4.18 (m , 2H), 2.62-2.46 (m, 2H), 2.25-2.05 (m, 1H), 1.95-1.85 (m, 1H), 1.80-1.59 (m, 6H), 1.47 (s, 3H), 1.36 (s, 3H), 1.28 (t, J = 6.9 Hz, 3H), 1.24 (s, 3H), 1.08 (d, J = 6.6 Hz, 3H), 1.01 (d, J = 6.6 Hz, 3H), 0.98 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 194.6, 166.6, 158.0, 112.4, 82.8, 78.1, 61.0, 35.2, 33.8, 29.7, 28.2, 27.9, 26.1, 23.6, 22.3, 14.2.

HRMS (ES) *m/z* calcd for $C_{25}H_{36}NaO_5$, $[M+Na]^+$: 439.2460, found : 439.2482.

Compound 14:



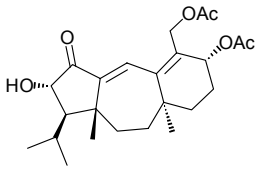
IR (thin film): ν_{max} 3398, 2927 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.17 (br s, 1H), 4.82 (d, J = 6.3 Hz, 1H), 4.41-4.36 (m, 3H), 4.17-4.11 (m, 1H), 2.40-2.30 (m, 1H), 2.10-1.90 (m, 1H), 1.73-1.57 (merged signals, 6H), 1.50 (s, 3H), 1.36 (s, 3H), 1.35-1.25 (m, 2H), 1.10 (s, 3H), 1.05 (d, J = 6.6 Hz, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 133.8, 111.8, 106.1, 83.0, 82.9, 69.0, 62.5, 36.3, 34.7, 28.3, 27.9, 27.5, 26.2, 24.1, 22.0, 21.9.

HRMS (ES) *m/z* calcd for $C_{23}H_{36}NaO_4$, $[M+Na]^+$: 399.2511, found : 399.2537.

Compound 18:



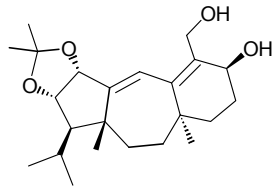
IR (thin film): ν_{max} 3457, 2937, 1741, 1718 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (s, 1H), 5.42 (br s, 1H), 4.54 (br s, 2H), 4.20 (d , J = 12.3 Hz, 1H), 2.07 (s , 3H), 2.04-1.90 (m, 3H), 1.98 (s, 3H), 1.85-1.76 (m, 3H), 1.65-1.52 (merged signals, 2H), 1.40-1.25 (m, 2H), 1.12 (d, J = 6.9 Hz, 3H), 1.10 (d, J = 6.9 Hz, 3H), 1.04 (s, 3H), 1.03 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 205.2, 170.7, 170.6, 140.6, 130.9, 77.8, 61.9, 36.1, 25.6, 24.7, 21.3, 20.7, 20.0, 15.4, 15.3.

HRMS (ES) *m/z* calcd for $C_{24}H_{34}NaO_6$, $[M+Na]^+$: 441.2253, found : 441.2270.

Compound 22:



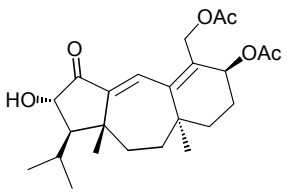
IR (thin film): ν_{max} 3388, 2928 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.08 (s, 1H), 4.86 (d, J = 6.3 Hz, 1H), 4.42-4.32 (m, 3H), 4.18-4.07 (m, 1H), 2.37 (br s, 1H), 2.06-2.04 (m, 1H), 1.89-1.68 (m, 4H), 1.58-1.50 (merged signals, 4H), 1.50 (s, 3H), 1.36 (s, 3H), 1.06 (d, J = 6.6 Hz, 3H), 1.00 (d, J = 6.6 Hz, 3H), 1.00 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 141.5, 111.9, 82.9, 28.3, 27.8, 27.6, 26.2, 26.0, 25.9, 25.8, 23.9, 22.1.

HRMS (ES) *m/z* calcd for $C_{23}H_{36}NaO_4$, $[M+Na]^+$: 399.2511, found : 399.2514

Compound 26:



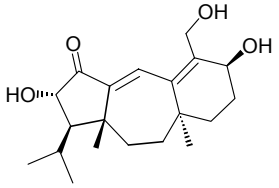
IR (thin film): ν_{max} 3448, 2935, 1742, 1732 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (s, 1H), 5.43 (br s, 1H), 4.54 (br s, 2H), 4.20 (d, J = 12.0 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 1.98-1.75 (series of m, 6H), 1.59-1.50 (merged signals, 4H), 1.13 (d, J = 6.8 Hz, 3H), 1.11 (d, J = 6.8 Hz, 3H), 1.07 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 205.1, 170.6, 170.5, 144.7, 138.8, 131.9, 43.1, 37.4, 25.6, 25.5, 24.6, 23.1, 21.2, 20.7, 20.1.

HRMS (ES) *m/z* calcd for $C_{24}H_{34}NaO_6$, $[M+Na]^+$: 441.2253, found : 441.2264.

Compound 2:



IR (thin film): ν_{max} 3419, 2921, 2853, 1743, cm^{-1}

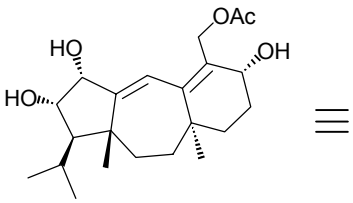
^{1}H NMR (500 MHz, $[D_6]$acetone, -10°C): δ 7.14 (s, 1H), 4.70-3.90 (series of m, 4H), 1.96-0.80 (series of multiplets, 10H), 1.09 (d, J = 6.5 Hz, 3H), 1.08 (d, J = 6.5 Hz, 3H), 1.02 (s, 3H), 0.93 (s, 3H).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (s, 1H), 4.48-4.44 (m, 1H), 4.35-4.30 (m, 2H), 4.19 (d, J = 12.6 Hz, 1H), 2.18-0.85 (series of multiplets, 10H), 1.12 (d, J = 6.6 Hz, 3H), 1.10 (d, J = 6.6 Hz, 3H), 1.06 (s, 3H), 0.95 (s, 3H).

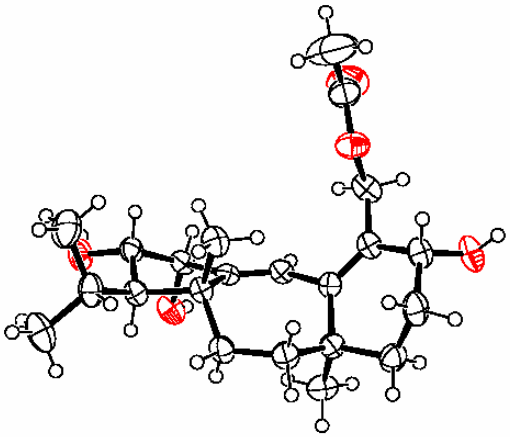
HRMS (ES) *m/z* calcd for $C_{20}H_{30}NaO_4$, $[M+Na]^+$: 357.2042, found : 357.2048.

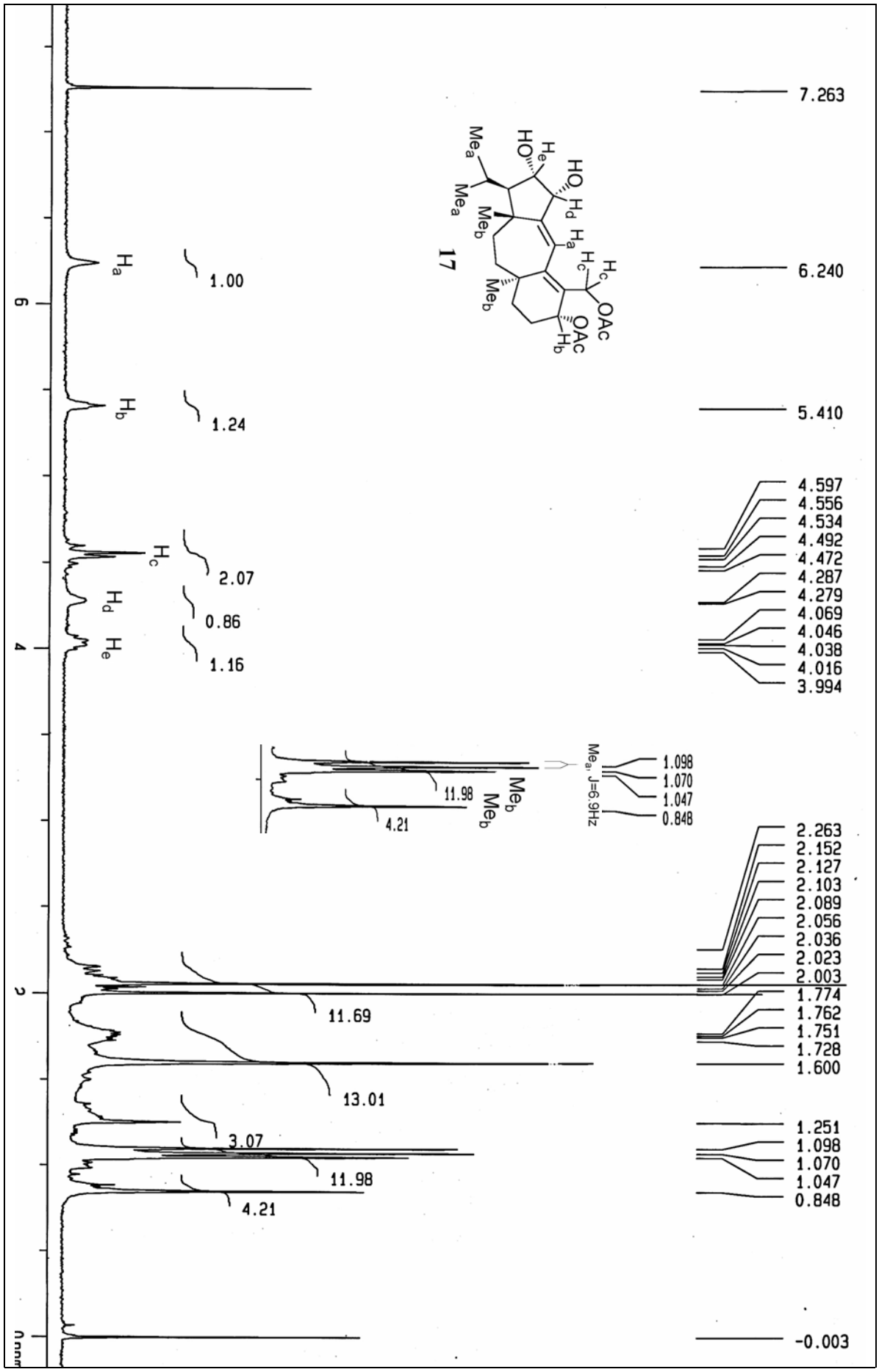
Crystal data for compound 16:

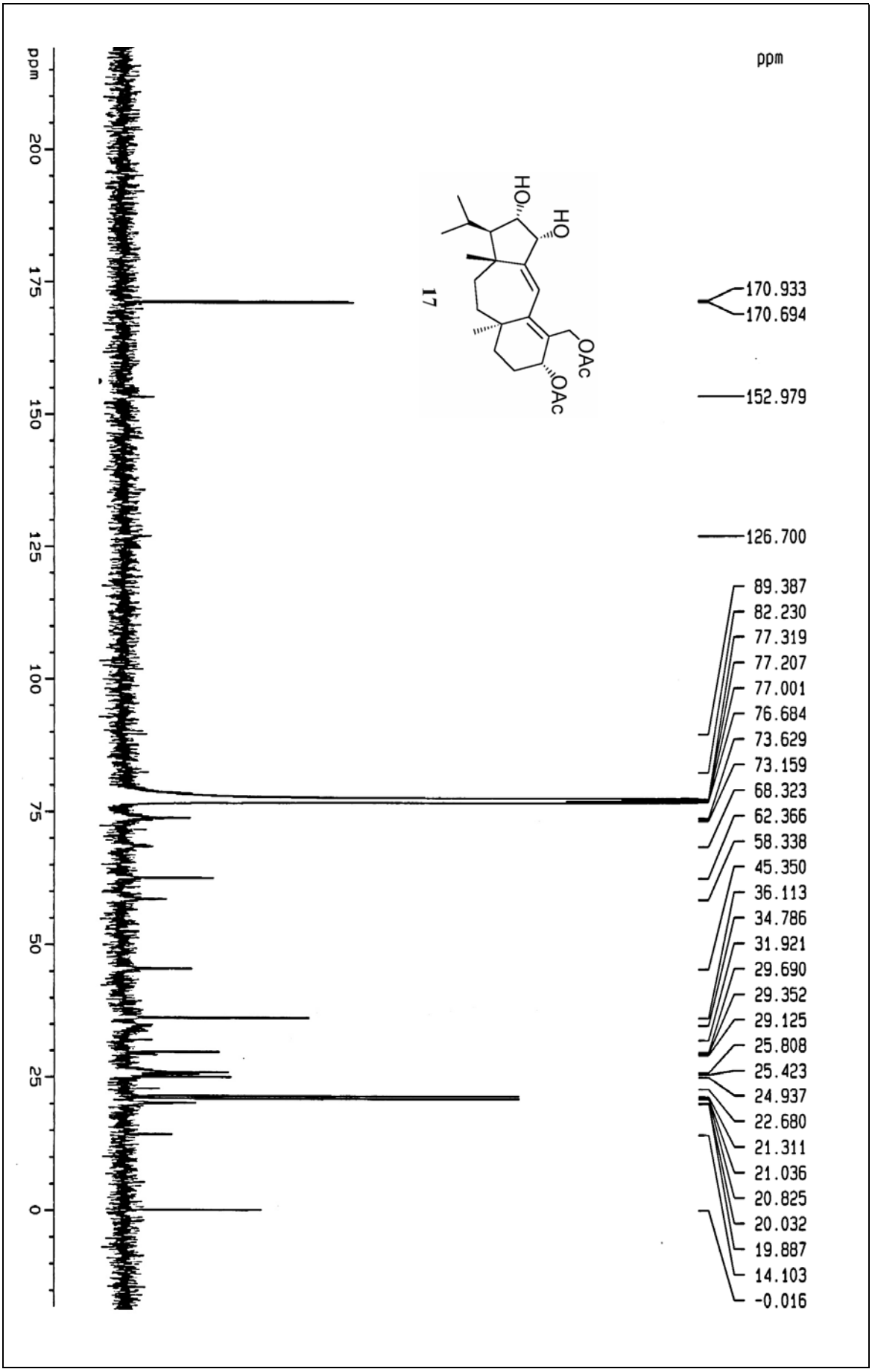
X-ray data were collected on a SMART CCD–BRUKER diffractometer with graphite monochromated MoK_α radiation (λ=0.7103Å). The structures were solved by direct methods (SIR92). Refinement was by full-matrix least-squares procedures on F^2 using SHELXL-97. The CIF file have been submitted to the Cambridge Crystallographic Data Centre and assigned to the corresponding dipository number. Crystal data for compound **16**: $C_{22}H_{34}O_5$, M = 378.49, triclinic, space group P-1, a = 9.1602(16) Å, b = 10.6414(19) Å, c = 12.088(2) Å, α = 81.181(3)°, β = 80.027(3)°, γ = 66.679(3)°, V = 1061.0(3) $Å^3$, Z = 2, ρ_{calcd} = 1.185 gcm^{-3}, $F(000)$ = 412, μ = 0.082 mm^{-1}, T = 293 K, R = 0.052, R_w = 0.122, GOF = 1.083 for 3067 reflections with $I>2\sigma(I)$, CCDC-272916. An ORTEP diagram with 50% ellipsoidal probability has been shown below.


OAc
HO
OH
HO

≡




17
7.263
6.240
5.410
4.597
4.556
4.534
4.492
4.472
4.287
4.279
4.069
4.046
4.038
4.016
3.994
2.263
2.152
2.127
2.103
2.089
2.056
2.036
2.023
2.003
1.774
1.762
1.751
1.728
1.600
1.251
1.098
1.070
1.047
0.848
-0.003
1.00
1.24
2.07
0.86
1.16
11.69
13.01
3.07
11.98
4.21
Me_a, J=6.9Hz
Me_b


ppm
200
175
150
125
100
75
50
25
0
HO
HO
OAc
OAc
17
ppm
170.933
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152.979
126.700
89.387
82.230
77.319
77.207
77.001
76.684
73.629
73.159
68.323
62.366
58.338
45.350
36.113
34.786
31.921
29.690
29.352
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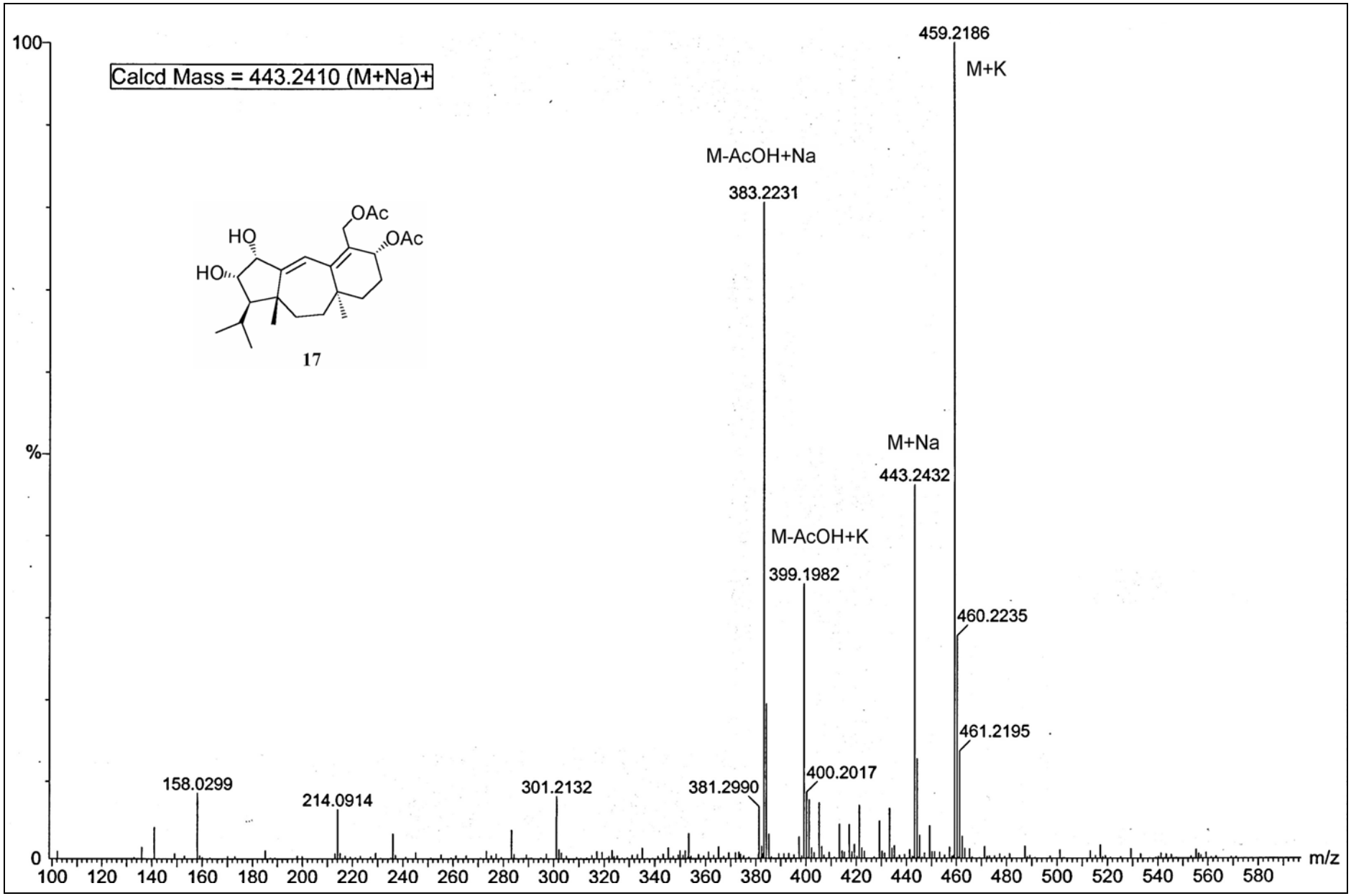
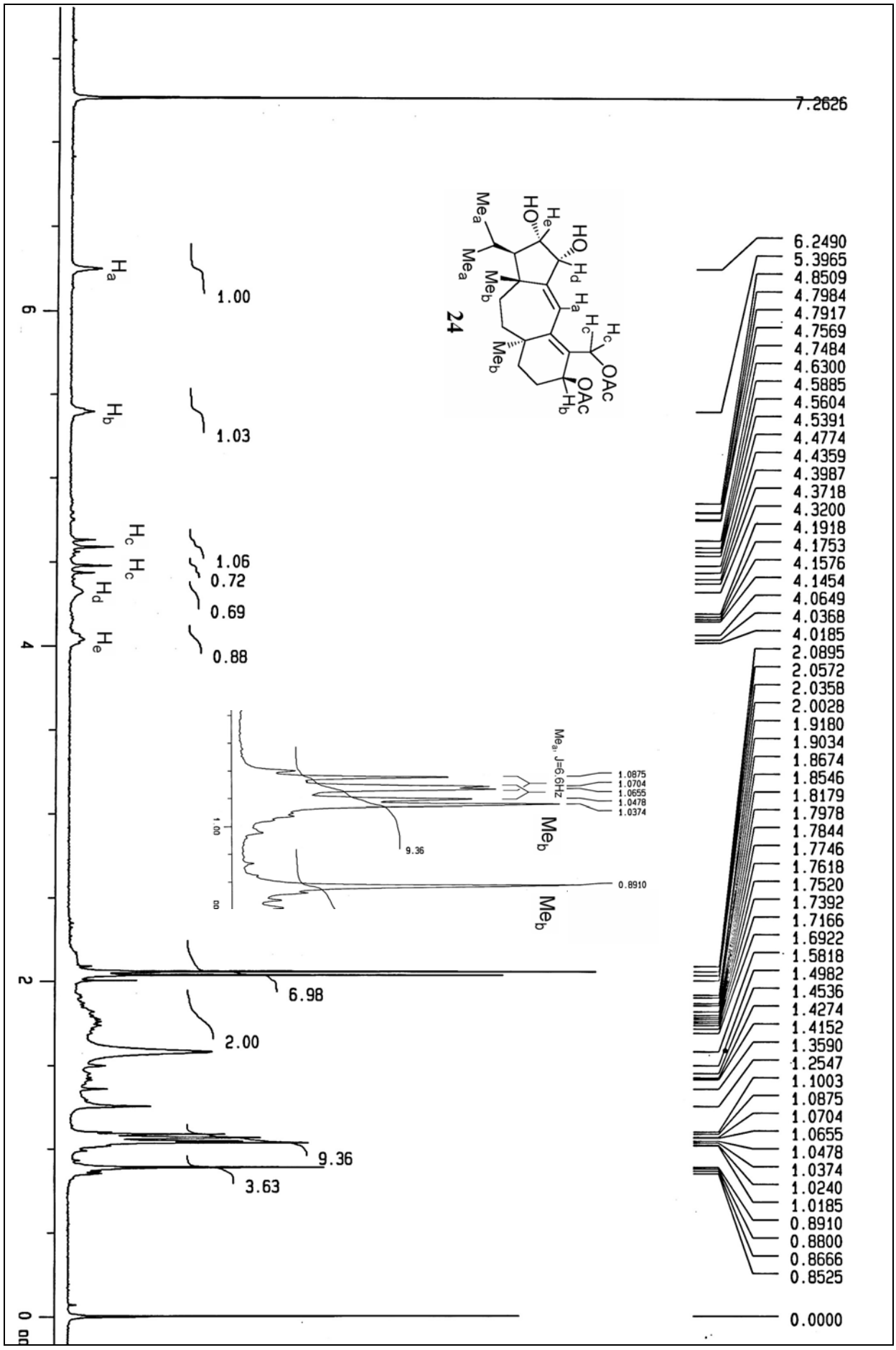
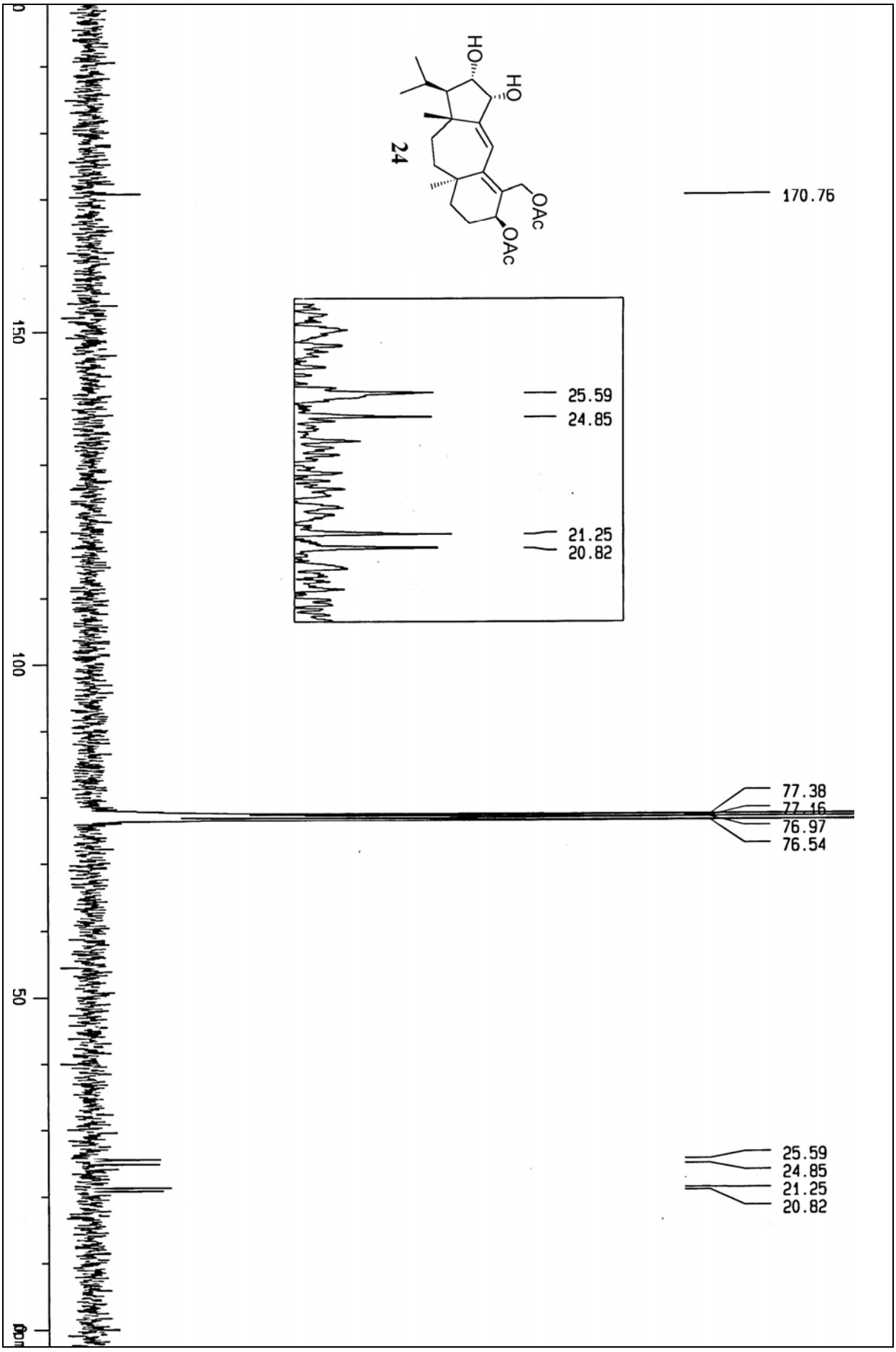
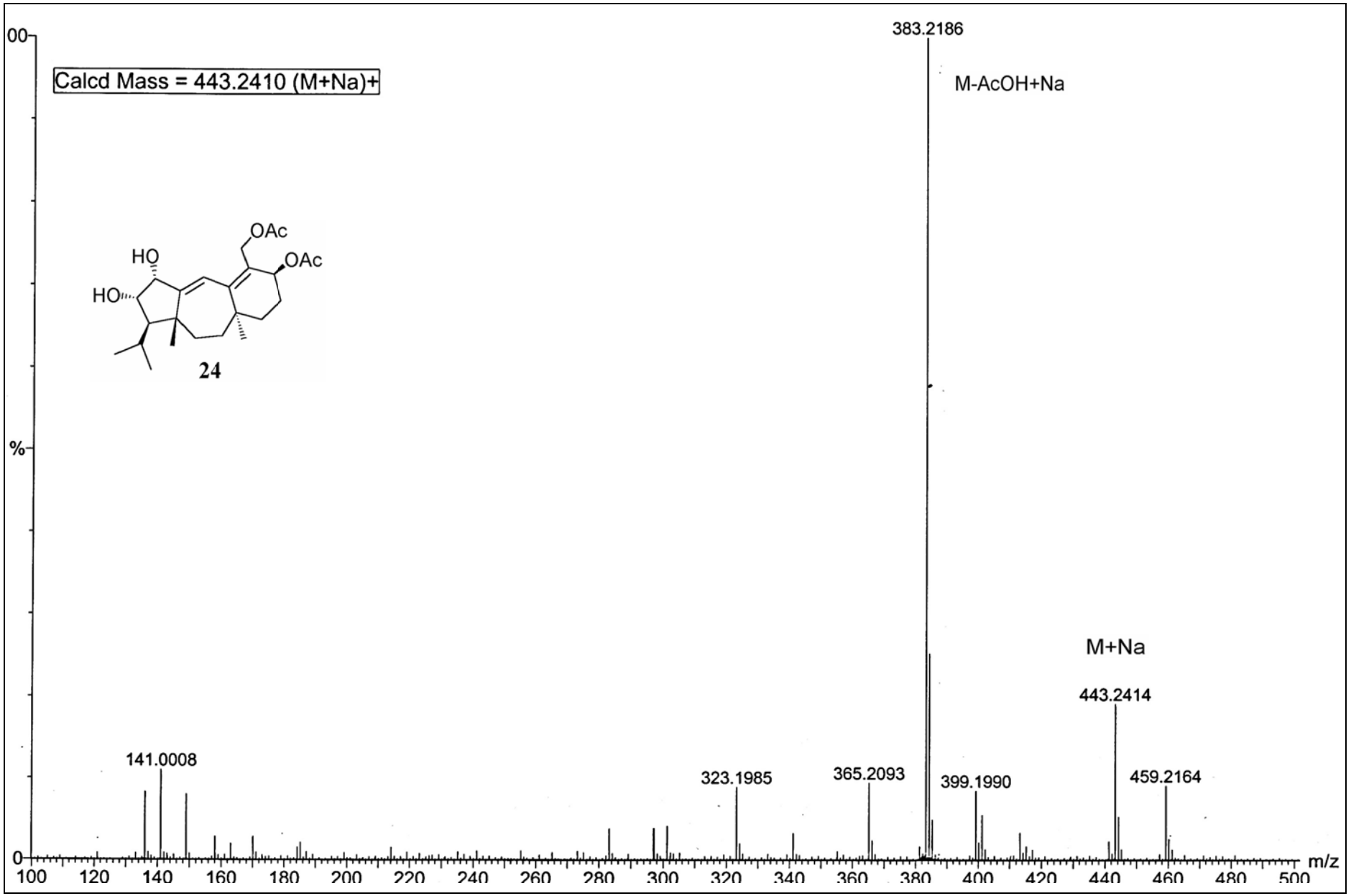
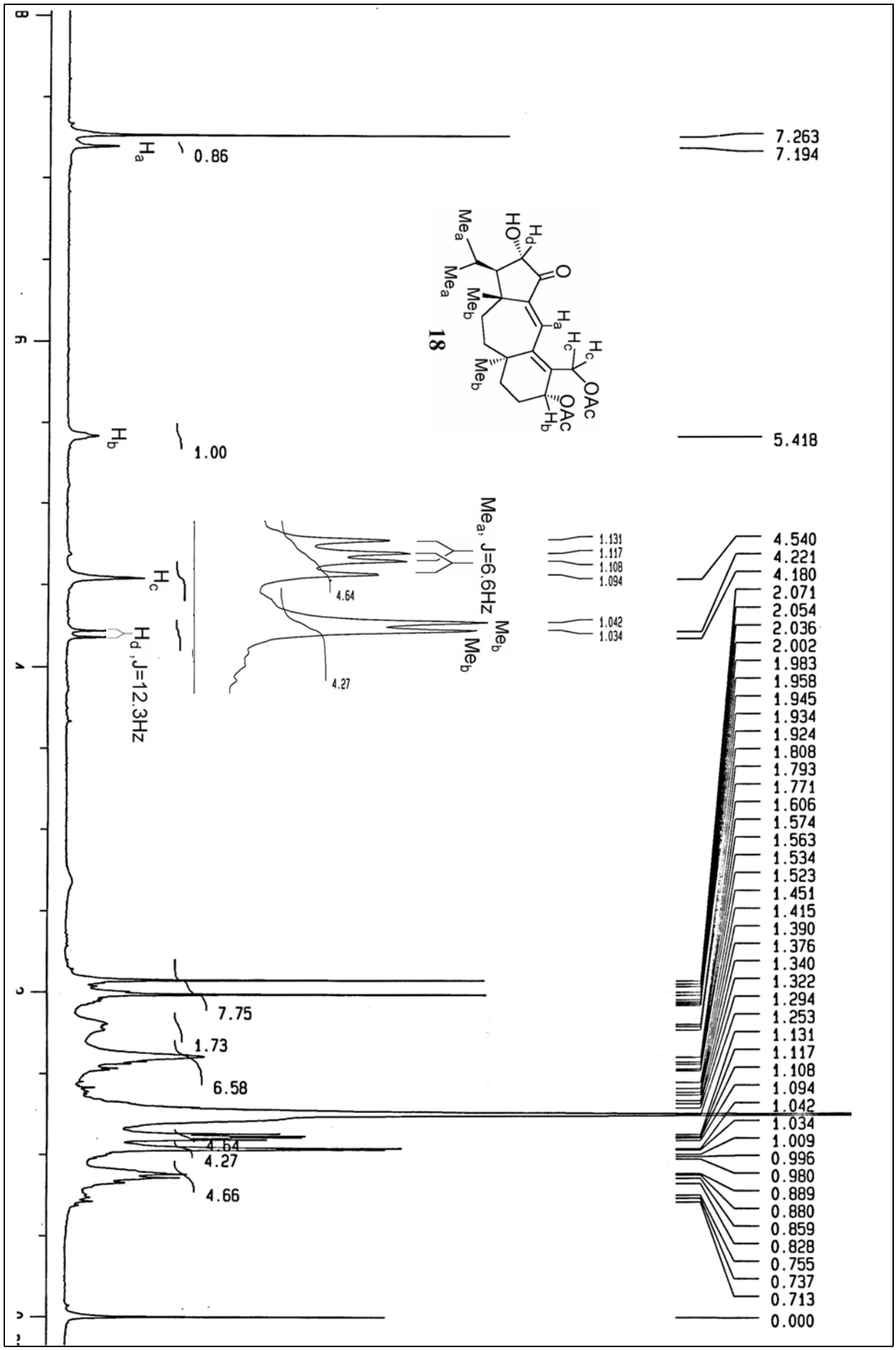
21.036
20.825
20.032
19.887
14.103
-0.016

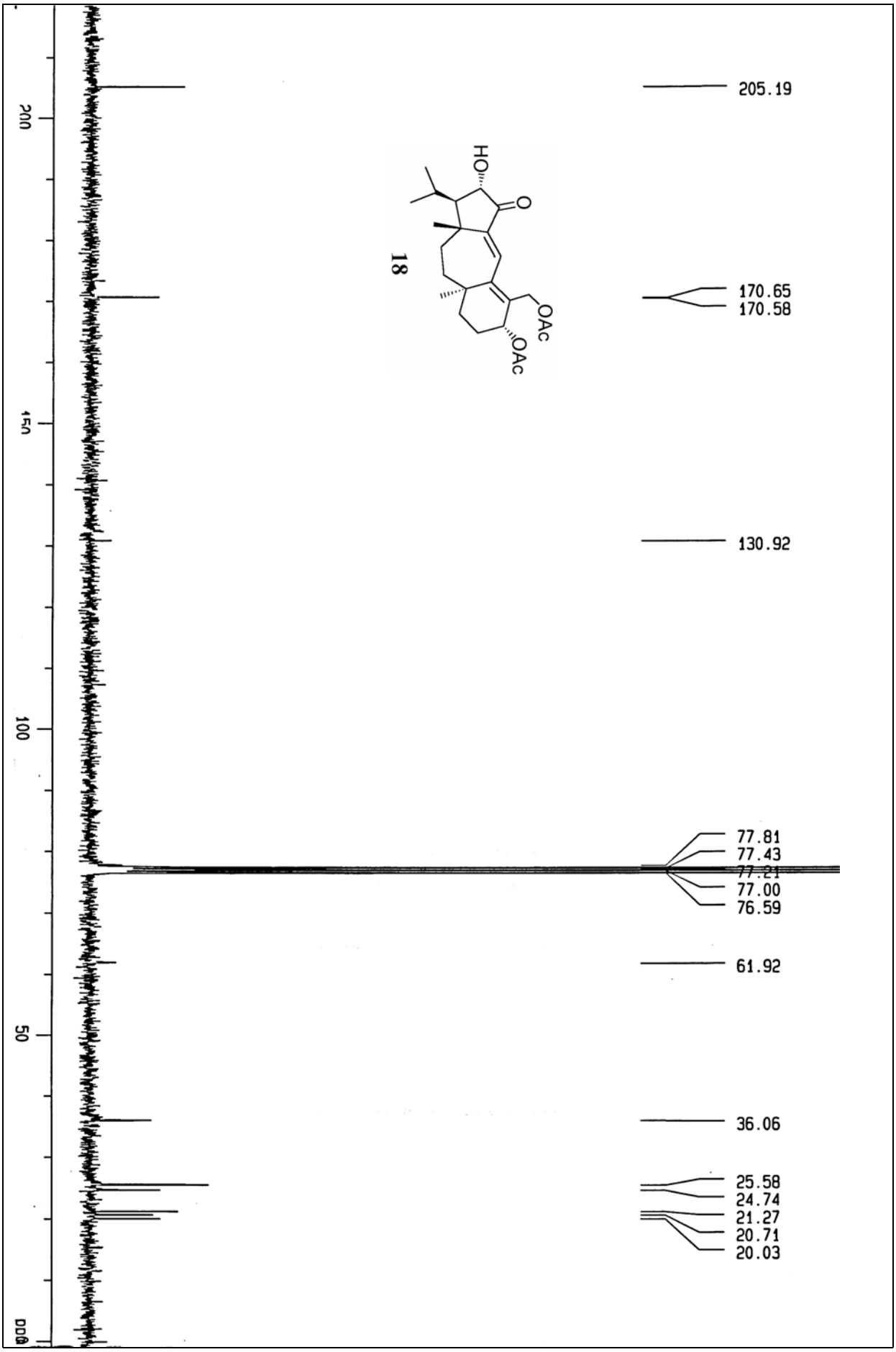

Calcd Mass = 443.2410 (M+Na)+
HO
HO
OAc
OAc
17
459.2186
M+K
M-AcOH+Na
383.2231
M+Na
443.2432
M-AcOH+K
399.1982
460.2235
461.2195
158.0299
214.0914
301.2132
381.2990
400.2017
100
%
0
m/z
100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580

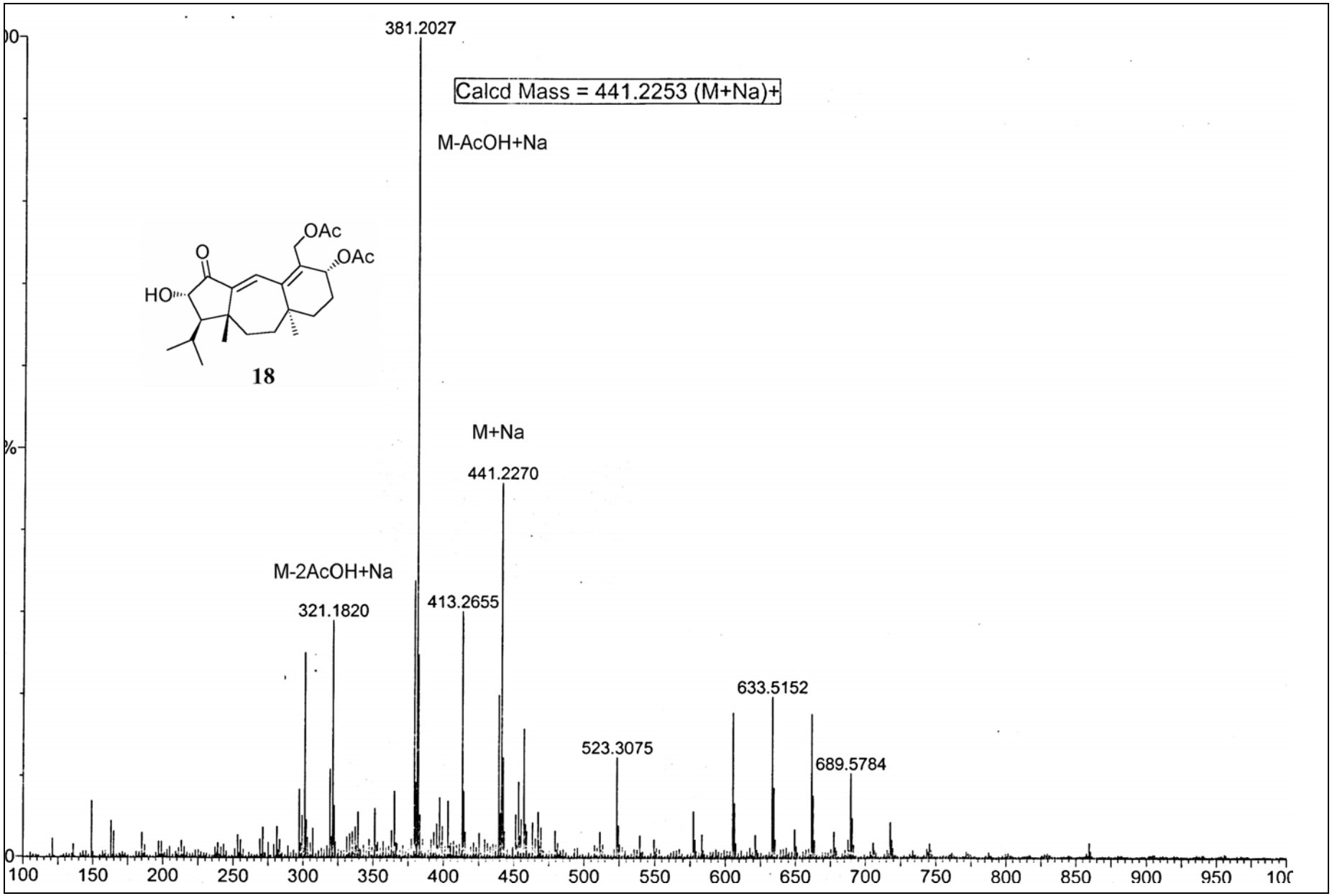

7.2626
6.2490
5.3965
4.8509
4.7984
4.7917
4.7569
4.7484
4.6300
4.5885
4.5604
4.5391
4.4774
4.4359
4.3987
4.3718
4.3200
4.1918
4.1753
4.1576
4.1454
4.0649
4.0368
4.0185
2.0895
2.0572
2.0358
2.0028
1.9180
1.9034
1.8674
1.8546
1.8179
1.7978
1.7844
1.7746
1.7618
1.7520
1.7392
1.7166
1.6922
1.5818
1.4982
1.4536
1.4274
1.4152
1.3590
1.2547
1.1003
1.0875
1.0704
1.0655
1.0478
1.0374
1.0240
1.0185
0.8910
0.8800
0.8666
0.8525
0.0000
24
Me_a
Me_b
H_a
H_b
H_c
H_d
H_e
HO
OAc
1.00
1.03
1.06
0.72
0.69
0.88
6.98
2.00
9.36
3.63
Me_a, J=6.6Hz
1.0875
1.0704
1.0655
1.0478
1.0374
0.8910
6
4
2
0

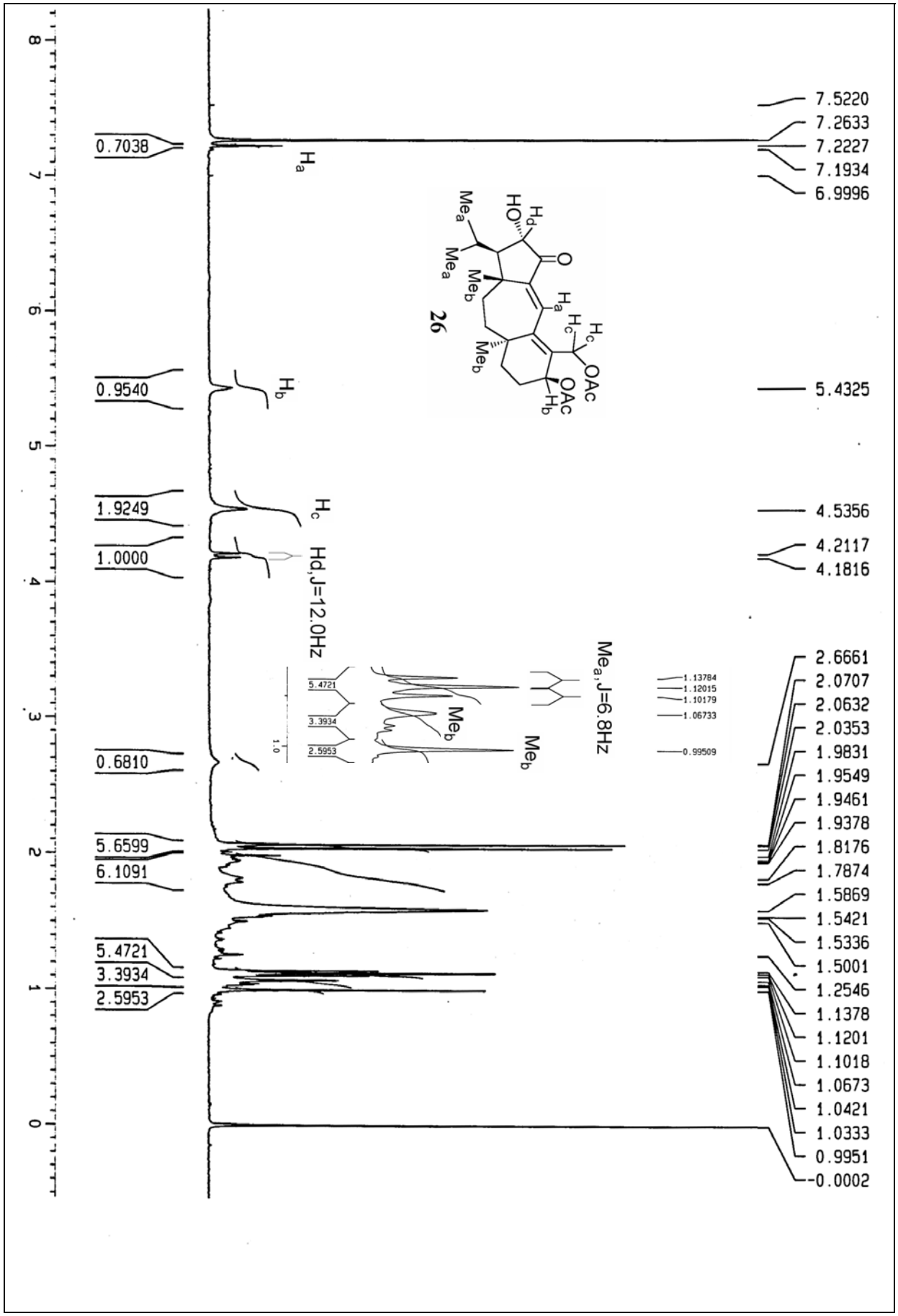

HO
HO
OAc
OAc
24
170.76
25.59
24.85
21.25
20.82
77.38
77.16
76.97
76.54
25.59
24.85
21.25
20.82
150
100
50
0

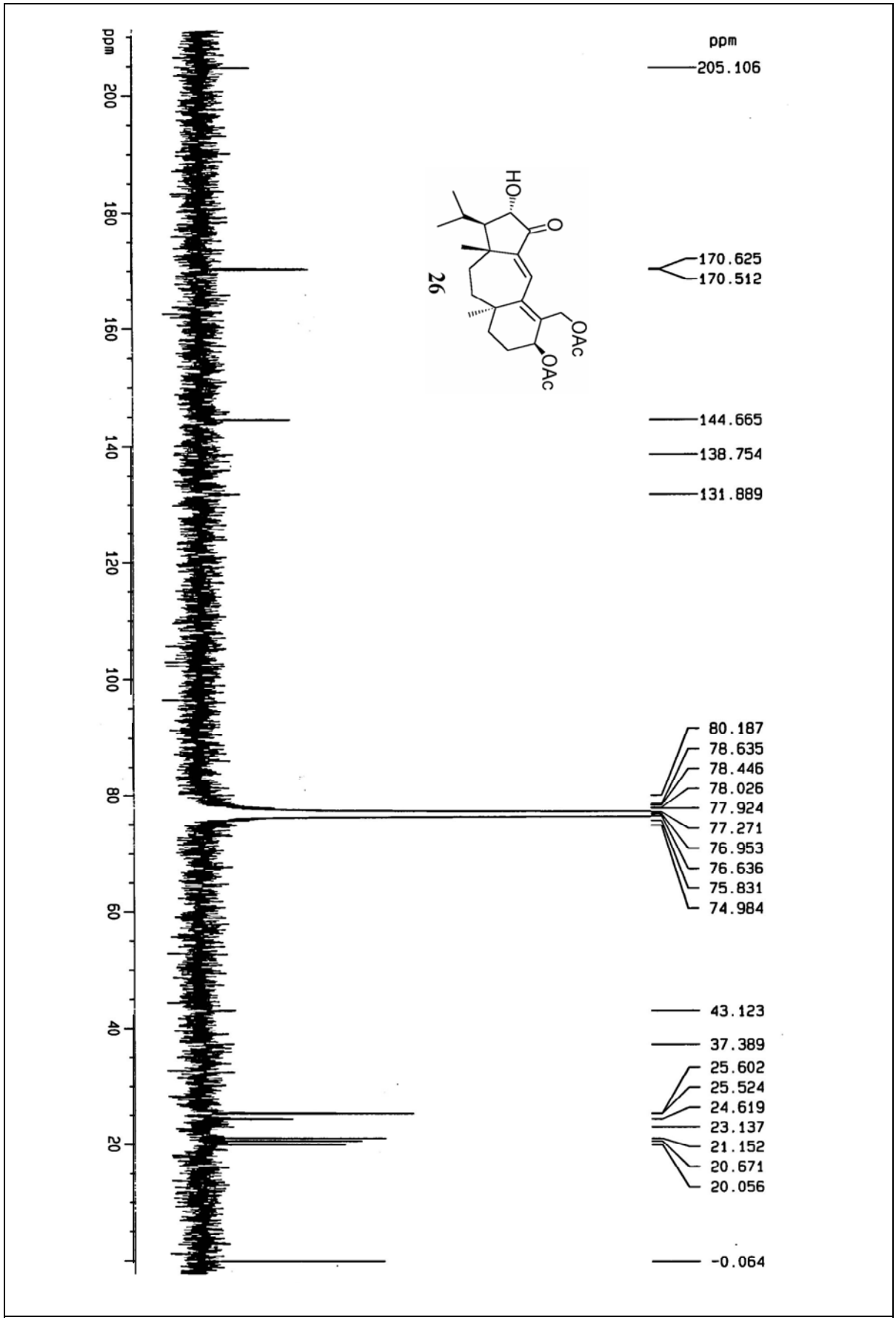

00
%
0
Calcd Mass = 443.2410 (M+Na)+
OAc
OAc
HO
HO
24
383.2186
M-AcOH+Na
M+Na
443.2414
141.0008
323.1985
365.2093
399.1990
459.2164
m/z
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500

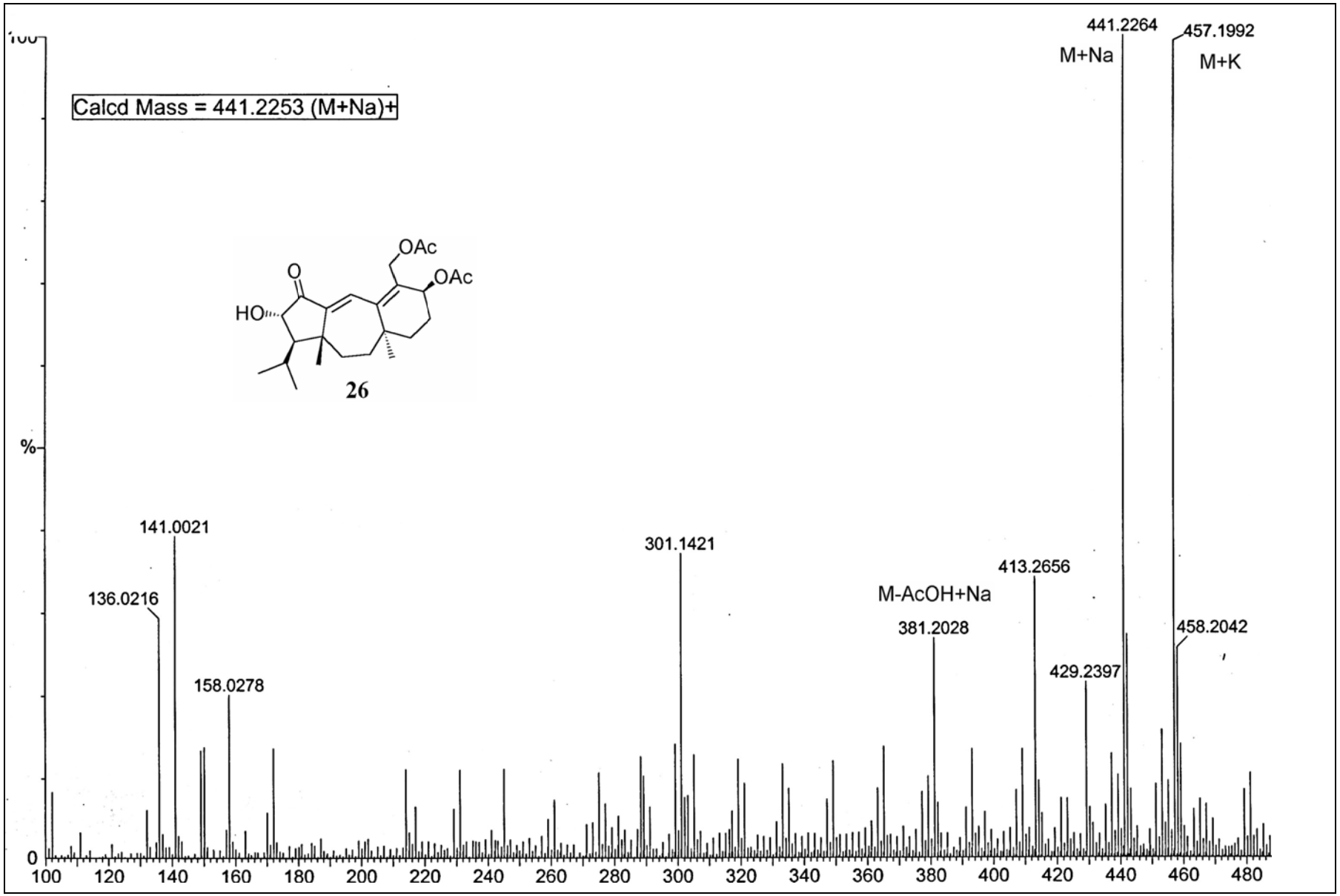

18
Ha
0.86
Hb
1.00
Hc
Hd ,J=12.3Hz
Mea, J=6.6Hz
Meb
Meb
7.75
1.73
6.58
4.64
4.27
4.66
7.263
7.194
5.418
4.540
4.221
4.180
2.071
2.054
2.036
2.002
1.983
1.958
1.945
1.934
1.924
1.808
1.793
1.771
1.606
1.574
1.563
1.534
1.523
1.451
1.415
1.390
1.376
1.340
1.322
1.294
1.253
1.131
1.117
1.108
1.094
1.042
1.034
1.009
0.996
0.980
0.889
0.880
0.859
0.828
0.755
0.737
0.713
0.000

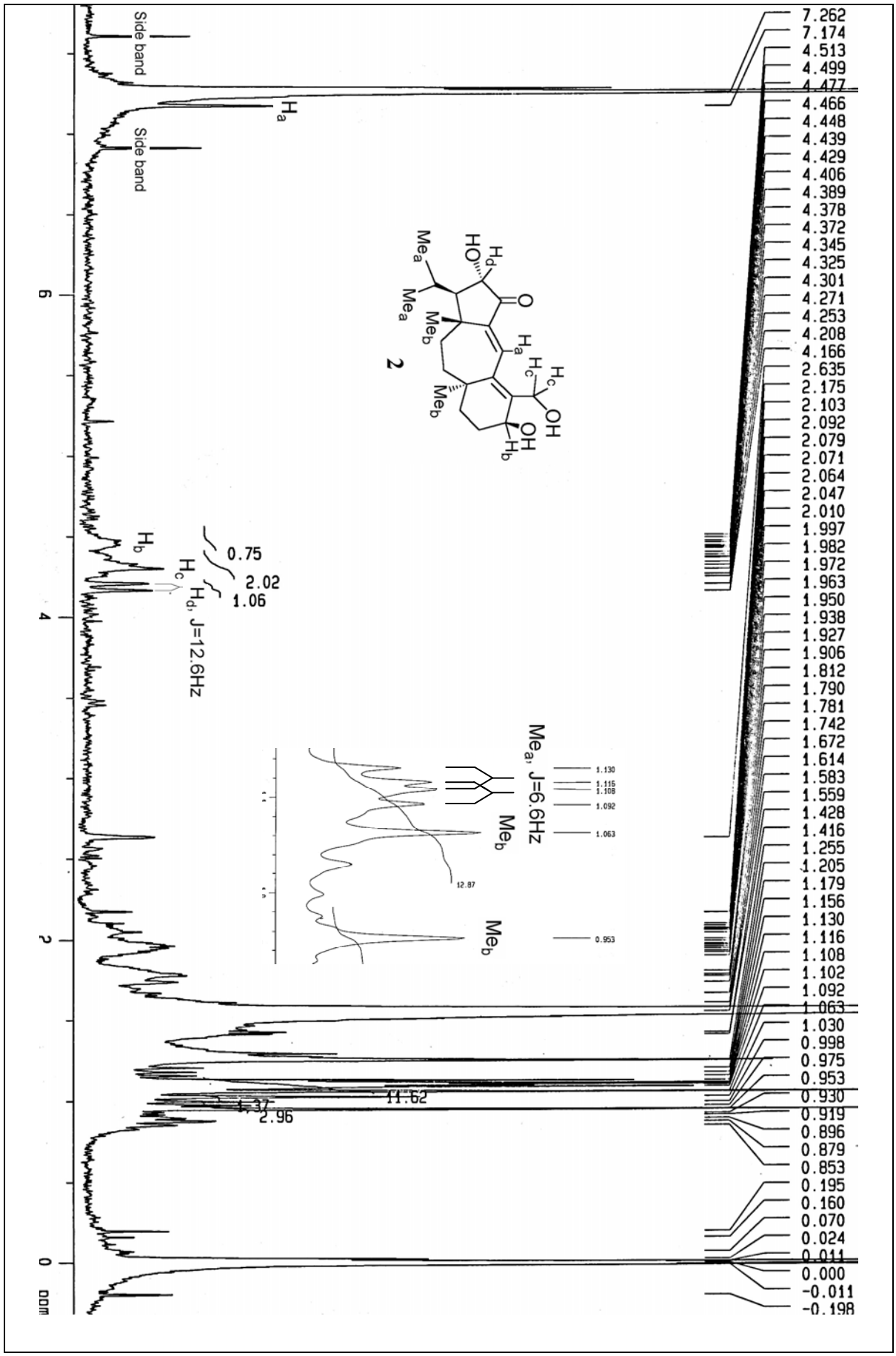

205.19
170.65
170.58
130.92
77.81
77.43
77.21
77.00
76.59
61.92
36.06
25.58
24.74
21.27
20.71
20.03
HO
O
OAc
OAc
18
200
150
100
50
0

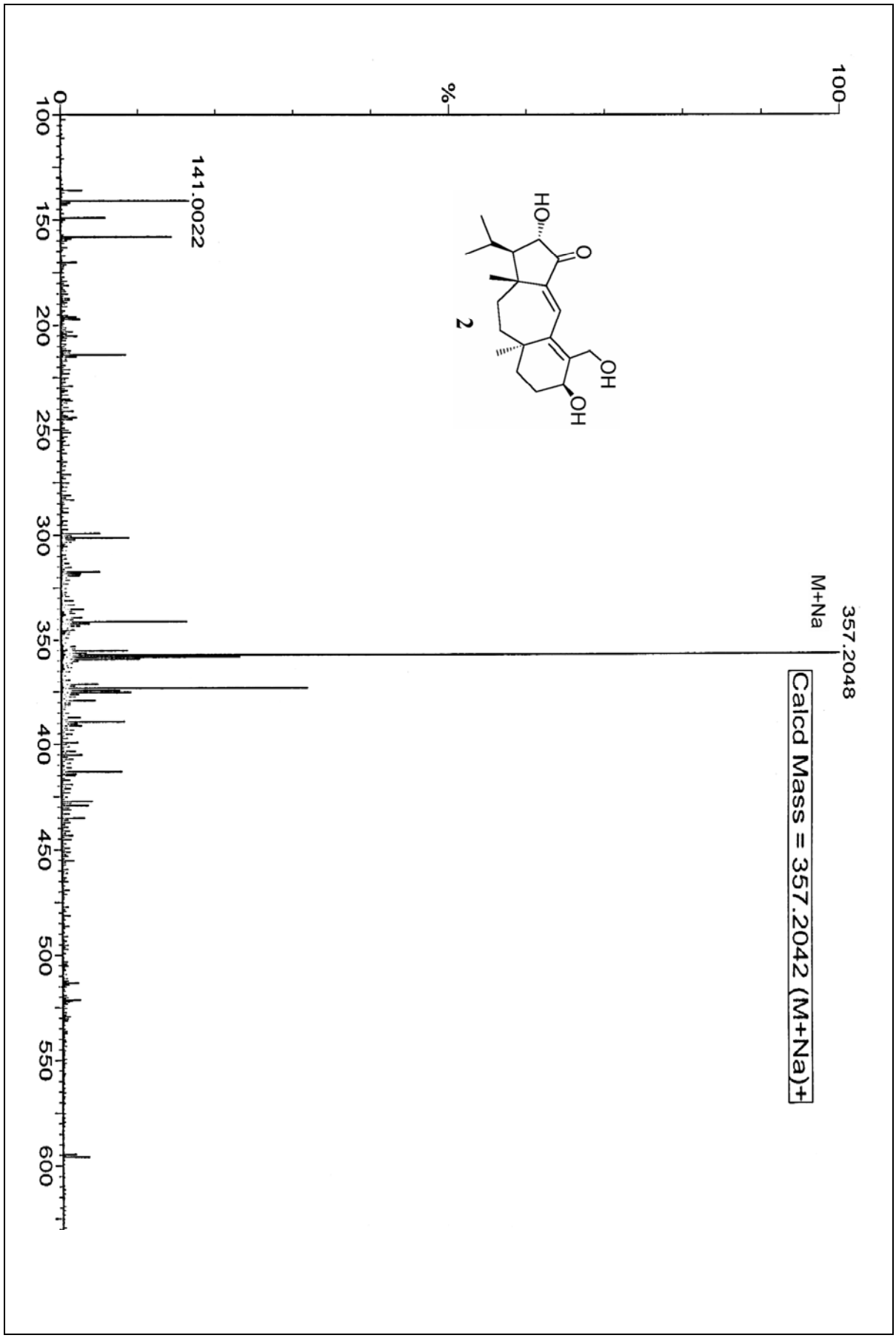

381.2027
Calcd Mass = 441.2253 (M+Na)+
M-AcOH+Na
OAc
OAc
O
HO
18
M+Na
441.2270
M-2AcOH+Na
321.1820
413.2655
633.5152
523.3075
689.5784
%
0
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950


7.5220
7.2633
7.2227
7.1934
6.9996
5.4325
4.5356
4.2117
4.1816
2.6661
2.0707
2.0632
2.0353
1.9831
1.9549
1.9461
1.9378
1.8176
1.7874
1.5869
1.5421
1.5336
1.5001
1.2546
1.1378
1.1201
1.1018
1.0673
1.0421
1.0333
0.9951
-0.0002
0.7038
0.9540
1.9249
1.0000
0.6810
5.6599
6.1091
5.4721
3.3934
2.5953
Ha
Hb
Hc
Hd,J=12.0Hz
Mea,J=6.8Hz
Meb
Mea
Meb
1.13784
1.12015
1.10179
1.06733
0.99509
5.4721
3.3934
2.5953
1.0
26


ppm
200
180
160
140
120
100
80
60
40
20
HO
O
OAc
OAc
26
ppm
205.106
170.625
170.512
144.665
138.754
131.889
80.187
78.635
78.446
78.026
77.924
77.271
76.953
76.636
75.831
74.984
43.123
37.389
25.602
25.524
24.619
23.137
21.152
20.671
20.056
-0.064


Calcd Mass = 441.2253 (M+Na)+
441.2264
M+Na
457.1992
M+K
OAc
OAc
O
HO
26
%
141.0021
136.0216
158.0278
301.1421
413.2656
M-AcOH+Na
381.2028
429.2397
458.2042
0
100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480


Side band
Side band
H_a
H_b
H_c
H_d, J=12.6Hz
0.75
2.02
1.06
Me_a, J=6.6Hz
Me_b
Me_b
11.62
1.37
2.96
12.87
1.130
1.116
1.108
1.092
1.063
0.953
2
Me_a
Me_a
Me_b
Me_b
H_a
H_b
H_c
H_d
HO
OH
OH
O
7.262
7.174
4.513
4.499
4.477
4.466
4.448
4.439
4.429
4.406
4.389
4.378
4.372
4.345
4.325
4.301
4.271
4.253
4.208
4.166
2.635
2.175
2.103
2.092
2.079
2.071
2.064
2.047
2.010
1.997
1.982
1.972
1.963
1.950
1.938
1.927
1.906
1.812
1.790
1.781
1.742
1.672
1.614
1.583
1.559
1.428
1.416
1.255
1.205
1.179
1.156
1.130
1.116
1.108
1.102
1.092
1.063
1.030
0.998
0.975
0.953
0.930
0.919
0.896
0.879
0.853
0.195
0.160
0.070
0.024
0.011
0.000
-0.011
-0.198
6
4
2
0
PPM


100
%
0
100
150
200
250
300
350
400
450
500
550
600
141.0022
357.2048
M+Na
Calcd Mass = 357.2042 (M+Na)+
HO
O
OH
OH
2