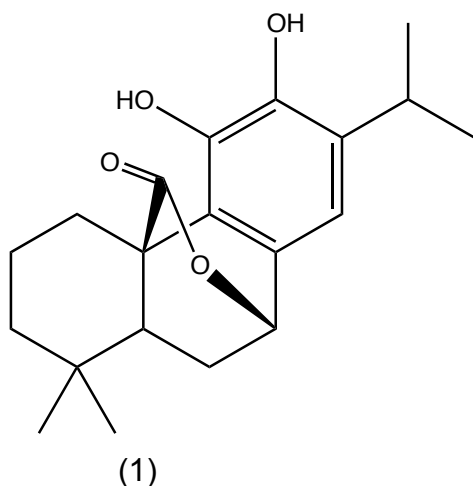


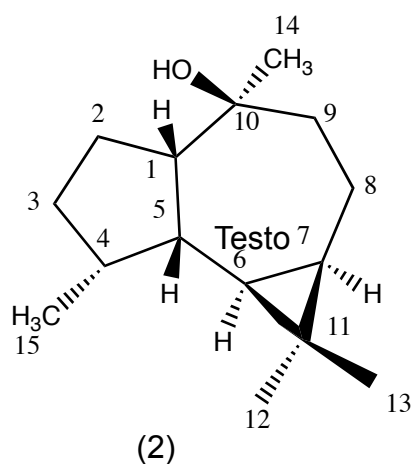
Spectroscopic data.

Carnosol (1)



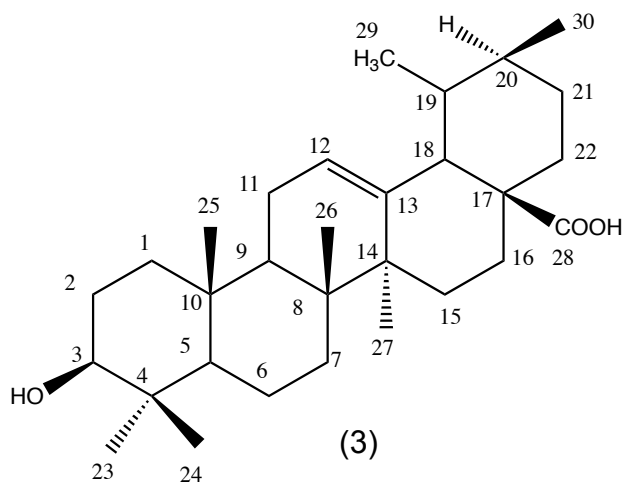
Colorless crystals, mp: 233-237°C, $[\alpha]_D^{20} = -51,9$ (c 0.05 in CHCl_3). The molecular formula $\text{C}_{20}\text{H}_{26}\text{O}_4$ was established from the MS (EI^+) M^+ at m/z 331.42 $[\text{M}+\text{H}]^+$. $^1\text{H-NMR}$ (CD_3OD , 200 MHz) δ 6.69 (H, s, H-14), 5.44 (1H, dd, $J = 3.8, 1.4$ Hz, H-7), 3.28 (1H, sept, $J = 6.8$, H-15), 2.65 (1H, dd, $J = 14, 1.6$ Hz, H-1 α), 2.49 (1H, ddd, $J = 14, 4.6$ Hz, H-1 β), 1.91 (1H, ddd, H-6 α), 1.6 (1H, m, H-6 β), 1.56 (1H, dd, $J = 10.6, 5.4$ Hz, H-5), 1.50 (1H, m, H-2 β), 1.42 (1H, dd, $J = 13, 1.4$ Hz, H-3 α), 1.21 (1H, ddd, $J = 13.4, 3.2$ Hz, H-3 β), 1.10 (2 \times 3H, d, $J = 6.8$, H₃-17, H₃-16), 0.87 (3H, s, H-18), 0.87 (3H, s, H-19).

Viridiflorol (2)



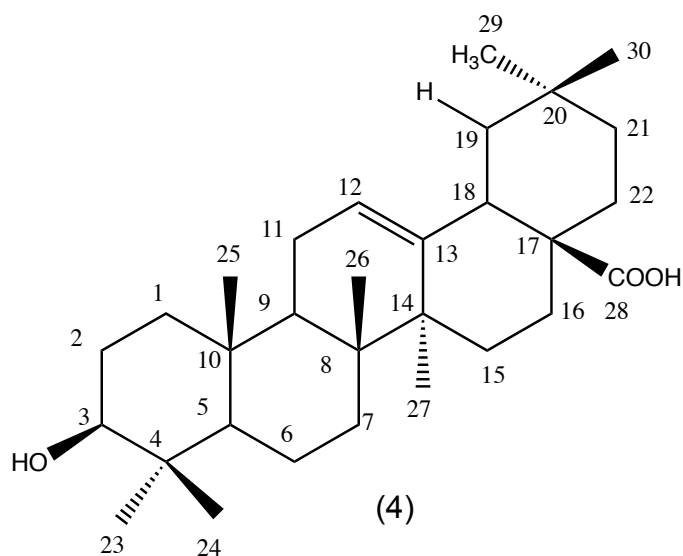
Colorless oil, $[\alpha]_D^{20} = +11.70$ (c 0.04 in CH_2Cl_2). The molecular formula $\text{C}_{15}\text{H}_{26}\text{O}$ was established from the MS (EI^+) M^+ at m/z 222.36. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 0.13 (1H, t, $J = 9,2$ Hz), 0.64 (1H, ddd, $J = 12, 9,6$ Hz), 0.93 (3H, d, $J = 6,6$ Hz), 1.01 (3H, s), 1.04 (3H, s), 1.18 (3H, s), 1.22-1.98 (12H, m). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ 74.6 (C-10), 58.2 (C-1), 39.7 (C-5), 38.5 (C-4), 37.8 (C-9), 32.1 (C-14), 29.1 (C-3), 28.7 (C-12), 28.6 (C-7), 25.8 (C-2), 22.3 (C-6), 18.8 (C-8), 18.4 (C-11), 16.3 (C-15), 16.1 (C-13).

Ursolic acid (3)



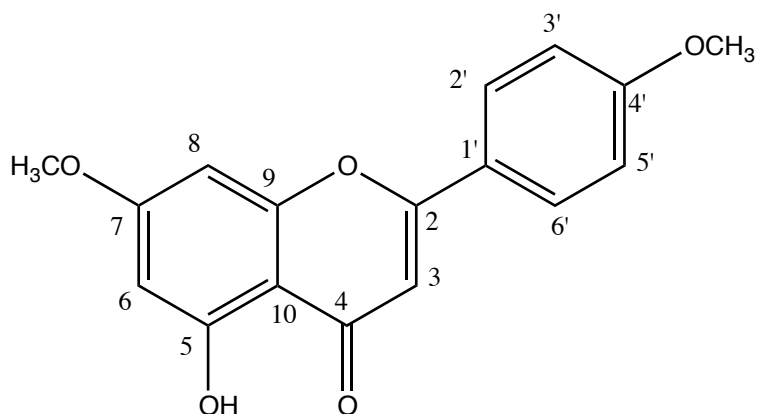
Whitish powder; mp: 210-221°C, $[\alpha]_{\text{D}}^{20} = +52.84$ (c 0.022 in MeOH)]. The molecular formula $\text{C}_{30}\text{H}_{48}\text{O}_3$ was established from the MS (EI^+) M^+ at m/z 457.79 $[\text{M}+\text{H}]^+$, 479.68 $[\text{M}+\text{Na}]^+$, 935.69 $[2\text{M}+\text{Na}]^+$. $^1\text{H-NMR}$ (CD_3COCD_3 , 300 MHz) δ 5.25 (H, t, $J = 3.4$ Hz, H-12), 2.91 (H, m, H-3), 2.09 (H, d, $J = 11.6$ Hz, H-18), 1.06 (3H, s, Me-27), 0.95 (3H, s, Me-23), 0.92 (3H, s, Me-26) 0.89 (3H, d, $J = 6$ Hz, H-30), 0.84 (3H, d, $J = 6$ Hz, H-29), 0.81 (3H, s, Me-24), 0.79 (3H, s, Me-25); $^{13}\text{C-NMR}$ (CD_3COCD_3 , 75 MHz) δ 179.3 (C-28), 139.7 (C-13), 123.4 (C-12), 78.8 (C-3), 56.6 (C-5), 54.2 (C-18), 48.9 (C-9), 48.8 (C-17), 42.6 (C-14), 39.8 (C-8), 39.7 (C-4), 38.2 (C-19), 38.1 (C-20), 37.9 (C-1), 37.0 (C-10), 36.8 (C-22), 31.6 (C-7), 29.6 (C-21), 29.1 (C-15), 28.0 (C-23), 27.4 (C-2), 24.3 (C-16), 23.7 (C-27), 23.3 (C-11), 21.5 (C-30), 18.4 (C-6), 17.5 (C-29), 17.4 (C-26), 16.7 (C-24), 16.2 (C-25).

Oleanolic acid (4)



Whitish powder; mp: $>300^{\circ}\text{C}$, $[\alpha]_{\text{D}}^{20} = +56.53$ (c 0.032 in MeOH)]. The molecular formula $\text{C}_{30}\text{H}_{48}\text{O}_3$ was established from the MS (EI^+) M^+ at m/z 457.92 $[\text{M}+\text{H}]^+$, 479.63 $[\text{M}+\text{Na}]^+$, 935.66 $[2\text{M}+\text{Na}]^+$. $^1\text{H-NMR}$ (CD_3OD , 300 MHz) δ 5.24 (H, t, H-12), 2.98 (H, t, H-3), 2.78 (H, dd, $J = 6.8, 4$ Hz, H-18), 0.98 (3H, s, Me-27), 0.89 (3H, s, Me-25), 0.86 (2 \times 3H, s, Me-30, 24), 0.83 (3H, s, H-29), 0.79 (3H, s, Me-26), 0.65 (3H, s, Me-23); $^{13}\text{C-NMR}$ (CD_3OD , 75 MHz) δ 181.8 (C-28), 145.4 (C-13), 123.8 (C-12), 79.9 (C-3), 56.9 (C-5), 48.9 (C-9), 48.5 (C-19), 43.4 (C-17), 40.9 (C-14), 40.6 (C-18), 40.2 (C-8), 39.9 (C-4), 38.3 (C-1), 37.0 (C-10), 33.8 (C-21), 33.3 (C-29), 32.9 (C-22), 32.5 (C-7), 30.8 (C-20), 28.7 (C-23), 27.6 (C-15), 27.4 (C-2), 26.0 (C-27), 23.8 (C-30), 23.3 (C-16), 23.1 (C-11), 17.9 (C-6), 17.8 (C-26), 16.5 (C-24), 16.1 (C-25).

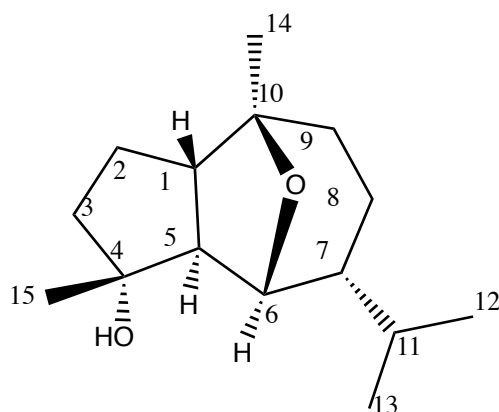
5-Hydroxy-4',7-dimethoxyflavone (5)



(5)

Yellow powder, mp: 216-218 °C. The molecular formula C₁₇H₁₄O₅ was established from the MS (EI⁺) M⁺ at *m/z* 298.08. ¹H-NMR (CDCl₃, 400 MHz) δ 12.81 (1H, s, OH-5), 7.84 (2H, d, *J*= 8 Hz, H-2',6'), 7.01 (2H, d, *J*= 8 Hz, H-3',5'), 6.57 (1H, s, H-3), 6.48 (1H, d, *J*= 2.2 Hz, H-6), 6.36 (1H, d, *J*= 4 Hz, H-8), 3.89 (3H, s), 3.88 (3H, s). ¹³C-NMR (CDCl₃, 100 MHz) δ ppm: 182.5 (C-4), 165.6 (C-7), 164.2 (C-2), 162.7 (C-5), 162.3 (C-4'), 157.8 (C-9), 128.2 (C-2',6'), 123.7 (C-1'), 114.6 (C-3',5'), 105.7 (C-10), 104.4 (C-3), 98.2 (C-6), 92.8 (C-8), 55.9 (7-OMe), 55.7 (4'-OMe).

Chrysothol (6)

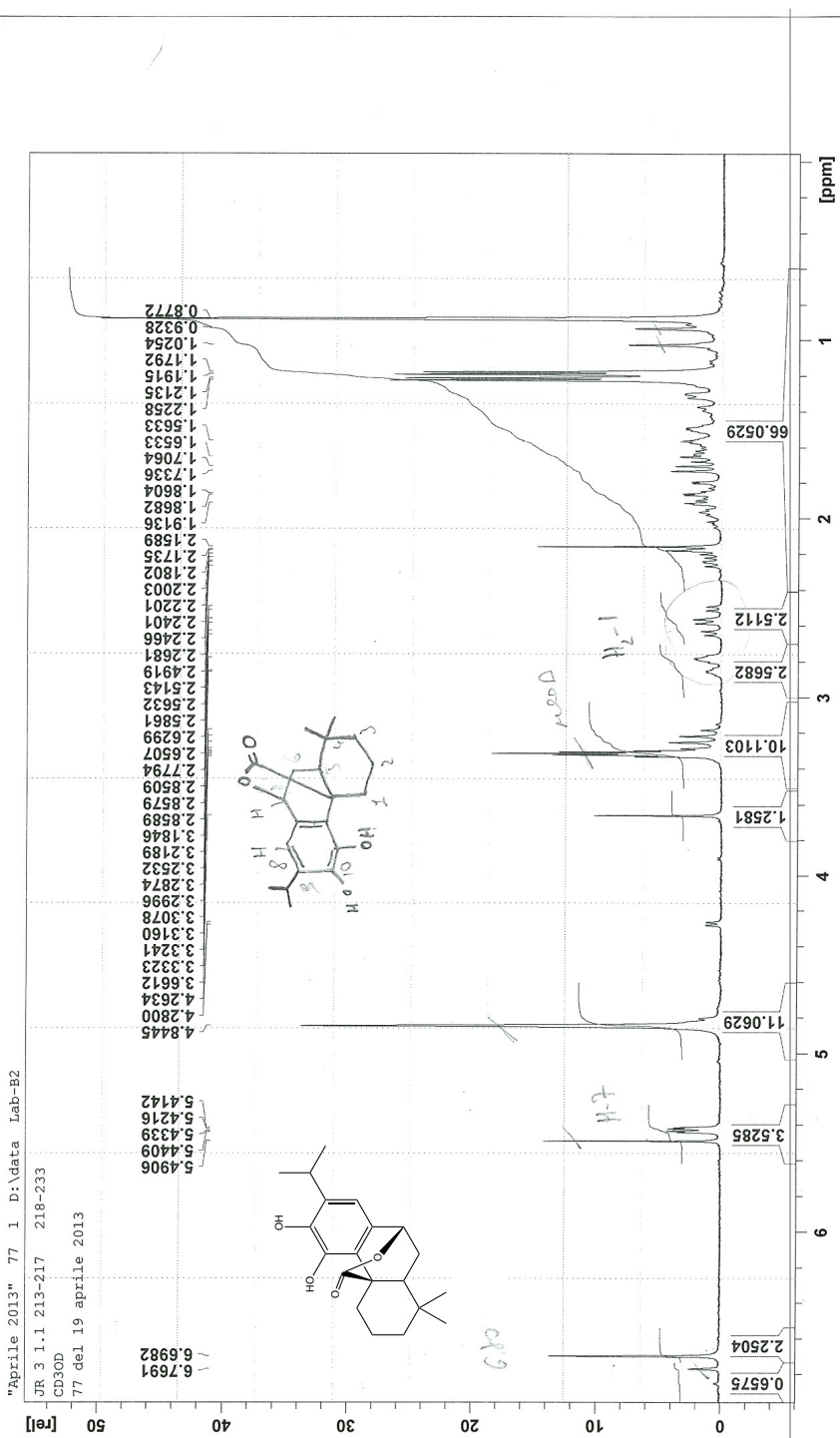


(6)

Colorless oil. The molecular formula $C_{15}H_{26}O_2$ was established from the MS (EI^+) M^+ at m/z 238.20. 1H -NMR ($CDCl_3$, 400 MHz) δ 3.94 (1H, d, $J = 4.0$ Hz), 2.26 (2H, m), 2.07 (2H, m), 1.68-1.48 (7H, m), 1.34 (2H, m), 1.35 (3H, s), 1.12 (3H, s), 0.87 (2 \times 3H, d, $J = 7.0$ Hz m). ^{13}C -NMR ($CDCl_3$, 100 MHz) δ 76.1 (C-6), 74.7 (C-4), 74.6 (C-10), 68.2 (C-5), 53.4 (C-1), 48.3 (C-3), 38.7 (C-7), 37.7 (C-9), 32.8 (C-11), 25.9 (C-15), 24.0 (C-2), 22.1 (C-14), 21.2 (C-12), 21.2 (C-13), 20.4 (C-8).

Supplementary material

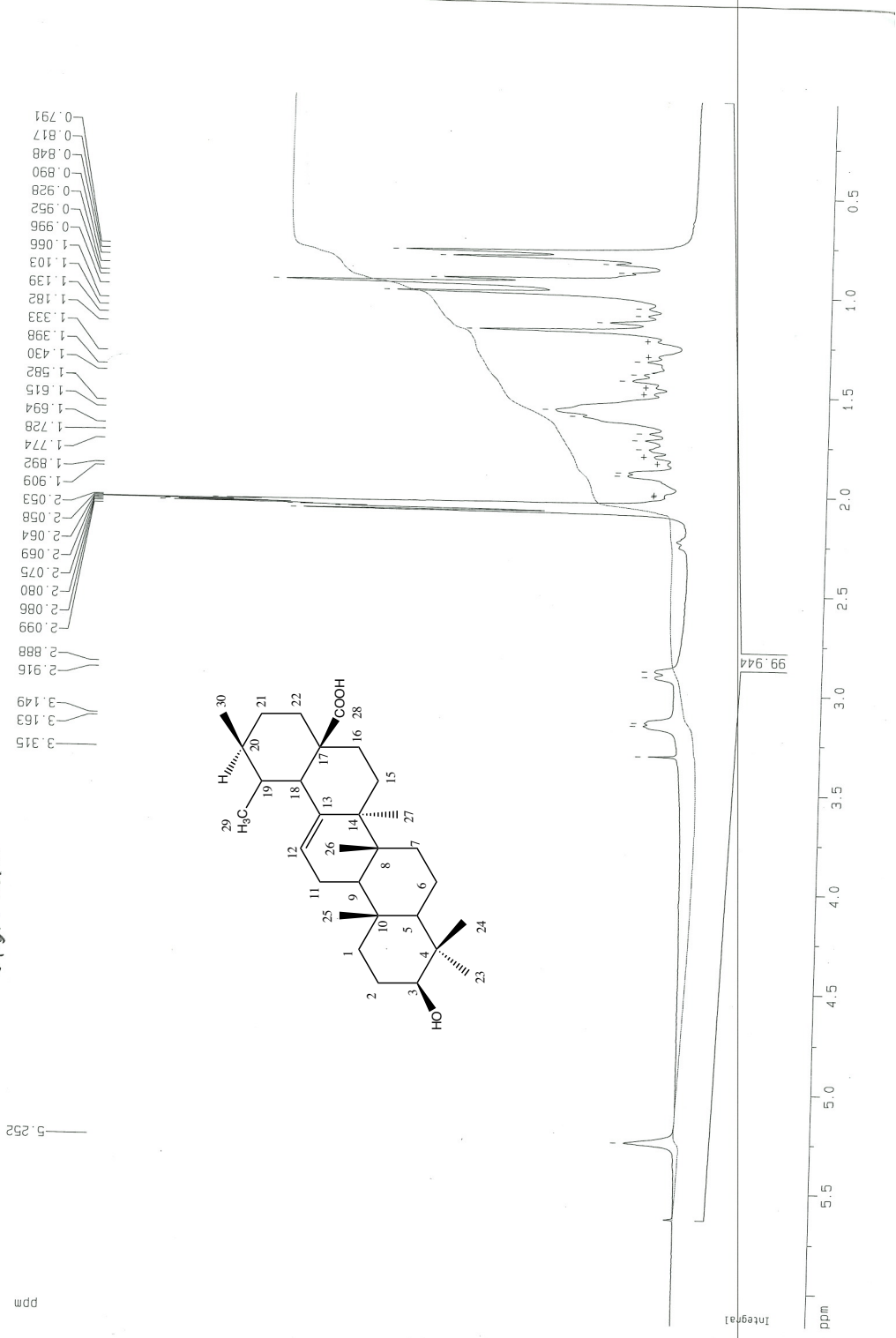
JR31.1 44/27



¹H-NMR (CDCl₃, 200 MHz) of carnosol.

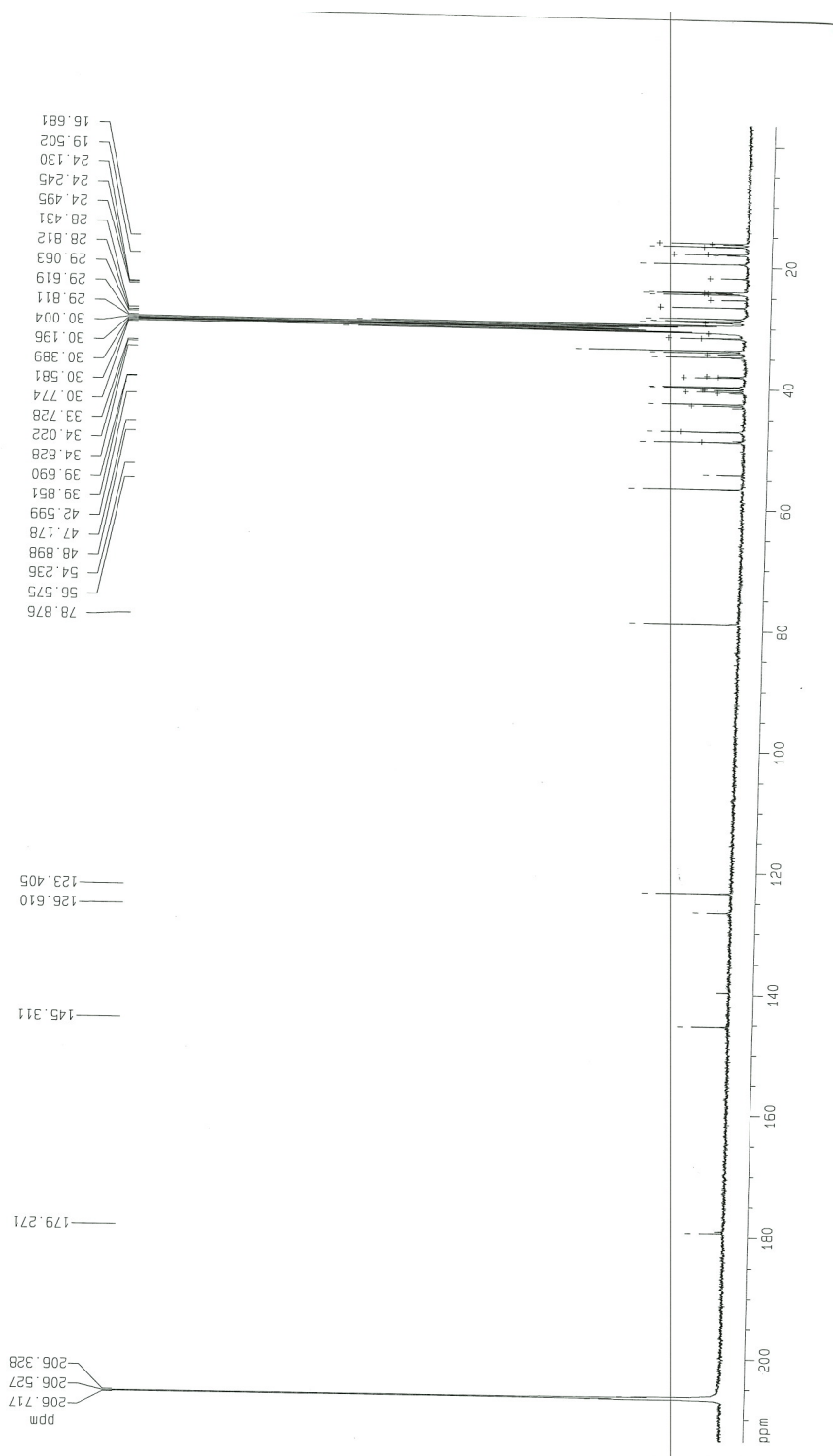
UR_3_1_1_19/22 cd3cocd3

JR311 23/25

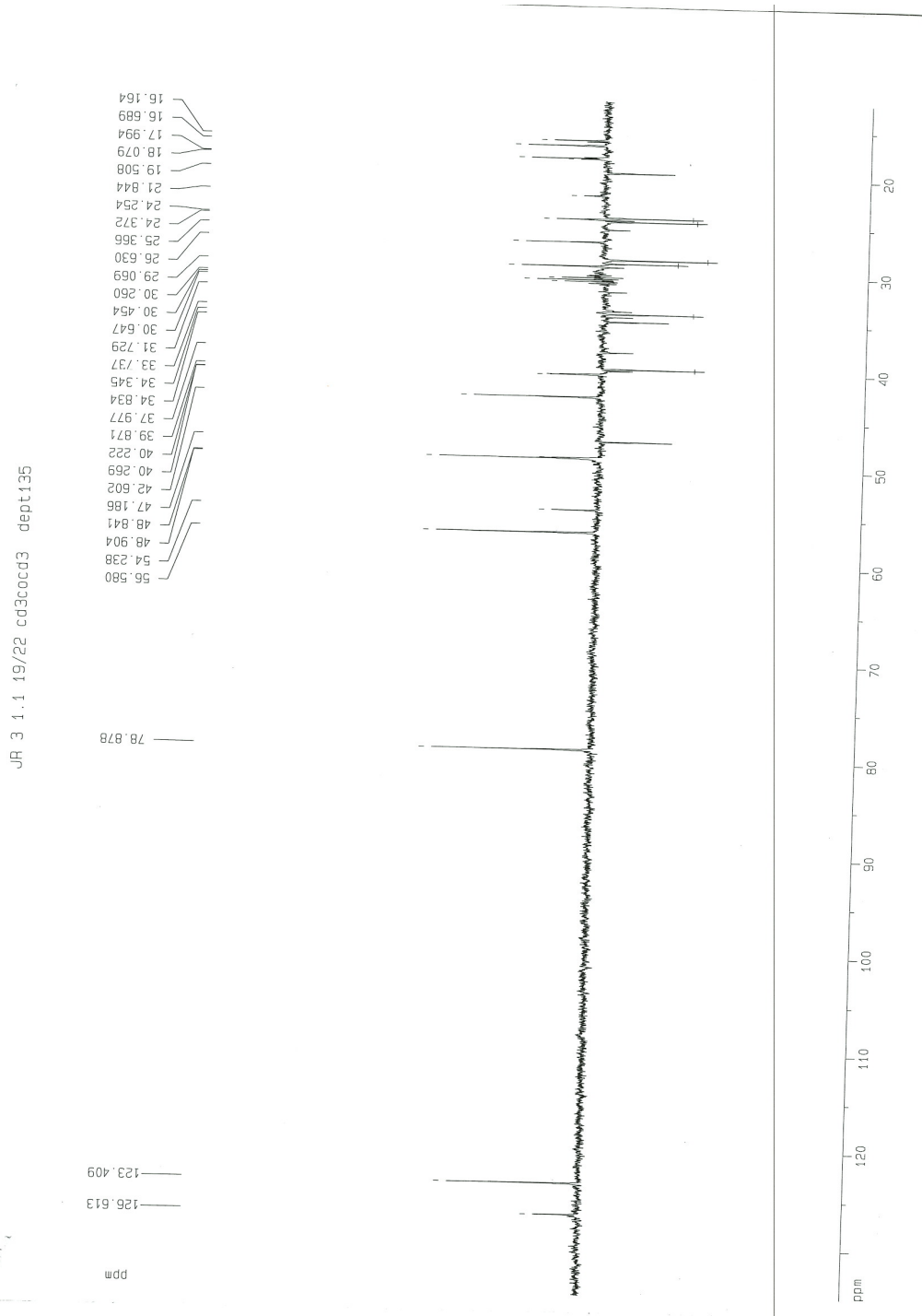


¹H-NMR of ursolic acid (CD₃COCD₃, 300 MHz)

JR_3_1_1.H22 cd3cocc3

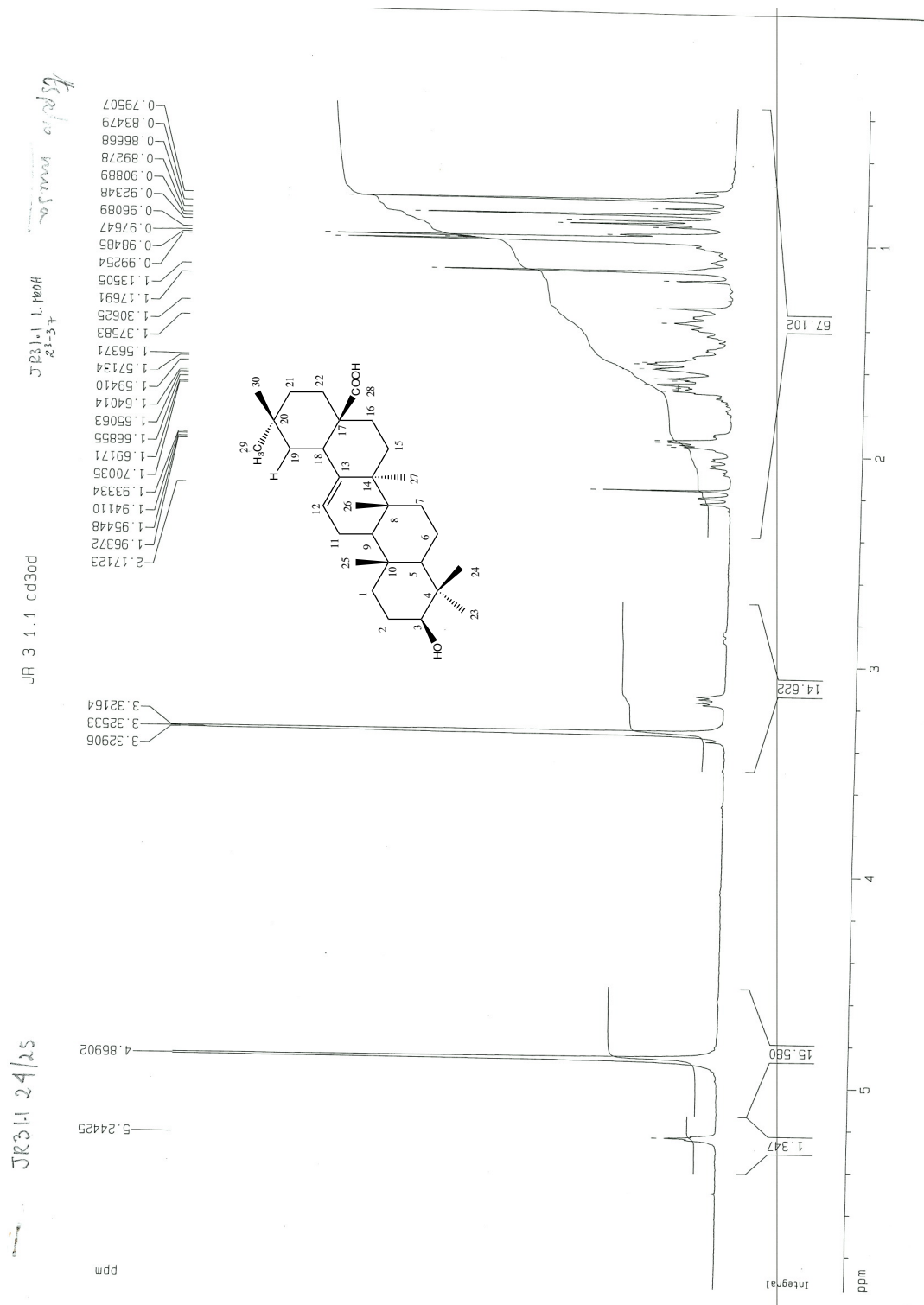


¹³C-NMR of ursolic acid (CD₃COCD₃, 75 MHz)

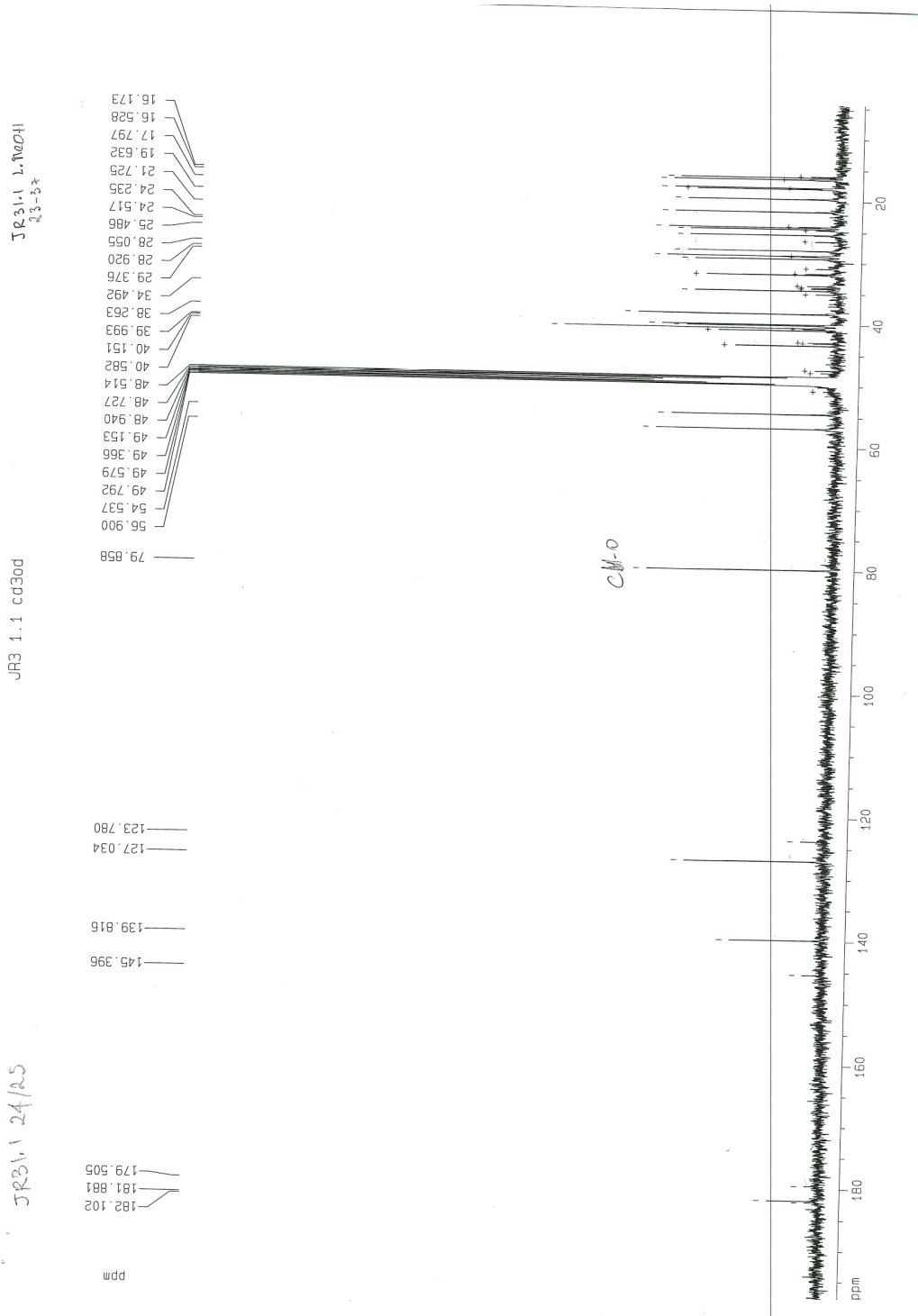


DEPT experiment (300 MHz) of ursolic acid in CD_3COCD_3 .

¹H-NMR of oleanolic acid (CD₃OD, 300 MHz)



¹³C-NMR of oleanolic acid (CD₃OD, 75 MHz)



JR31.1 1. hecH
23-34

JR3 1.1 cd3od dept135

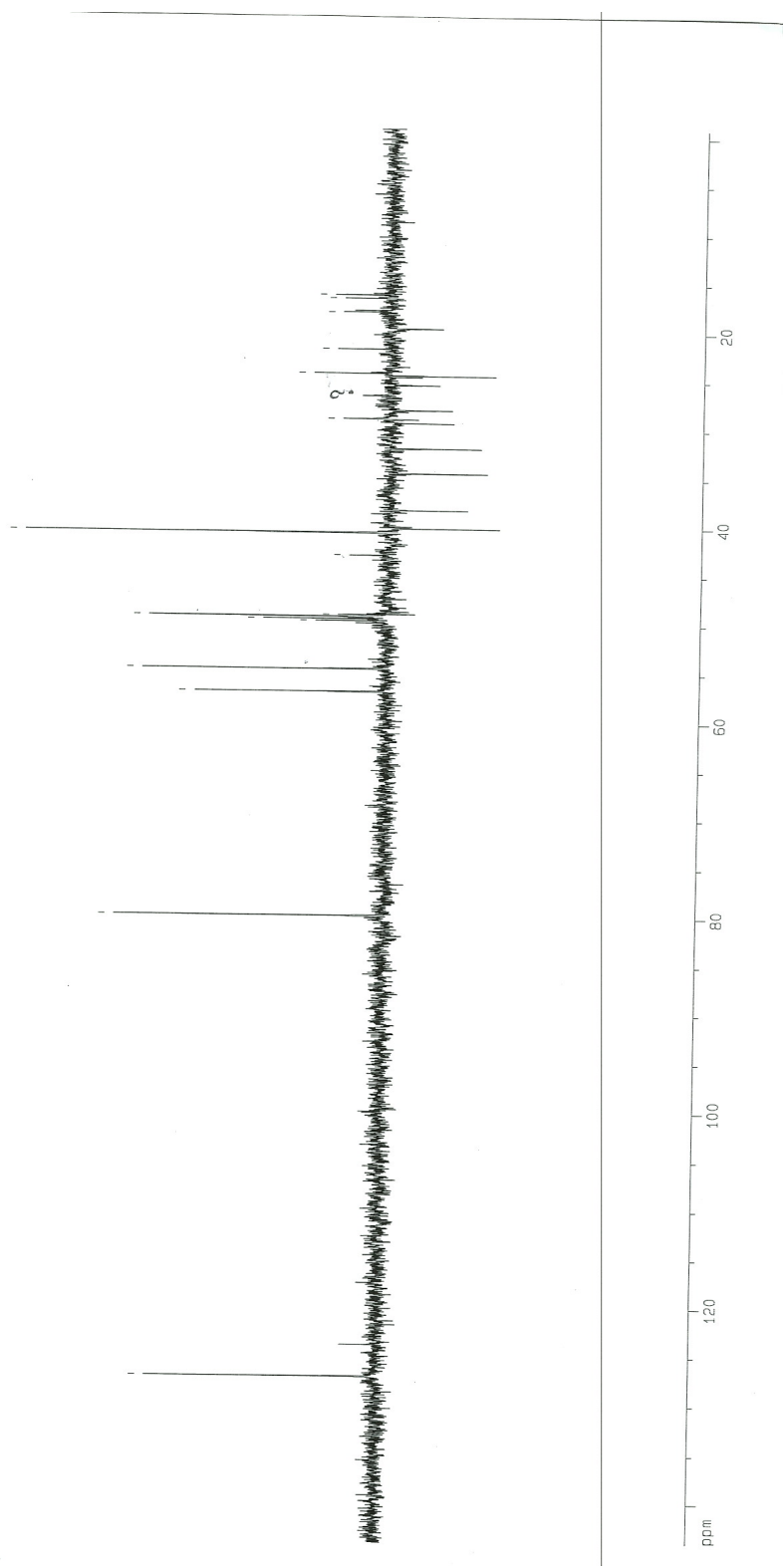
JR31.1 24/25

- 16.166
- 16.517
- 17.957
- 19.625
- 21.718
- 24.228
- 24.505
- 25.475
- 28.047
- 28.910
- 29.369
- 31.931
- 34.482
- 38.266
- 40.141
- 40.571
- 42.897
- 48.998
- 49.153
- 49.213
- 49.428
- 49.641
- 54.527
- 55.889

79.850

127.025

ppm

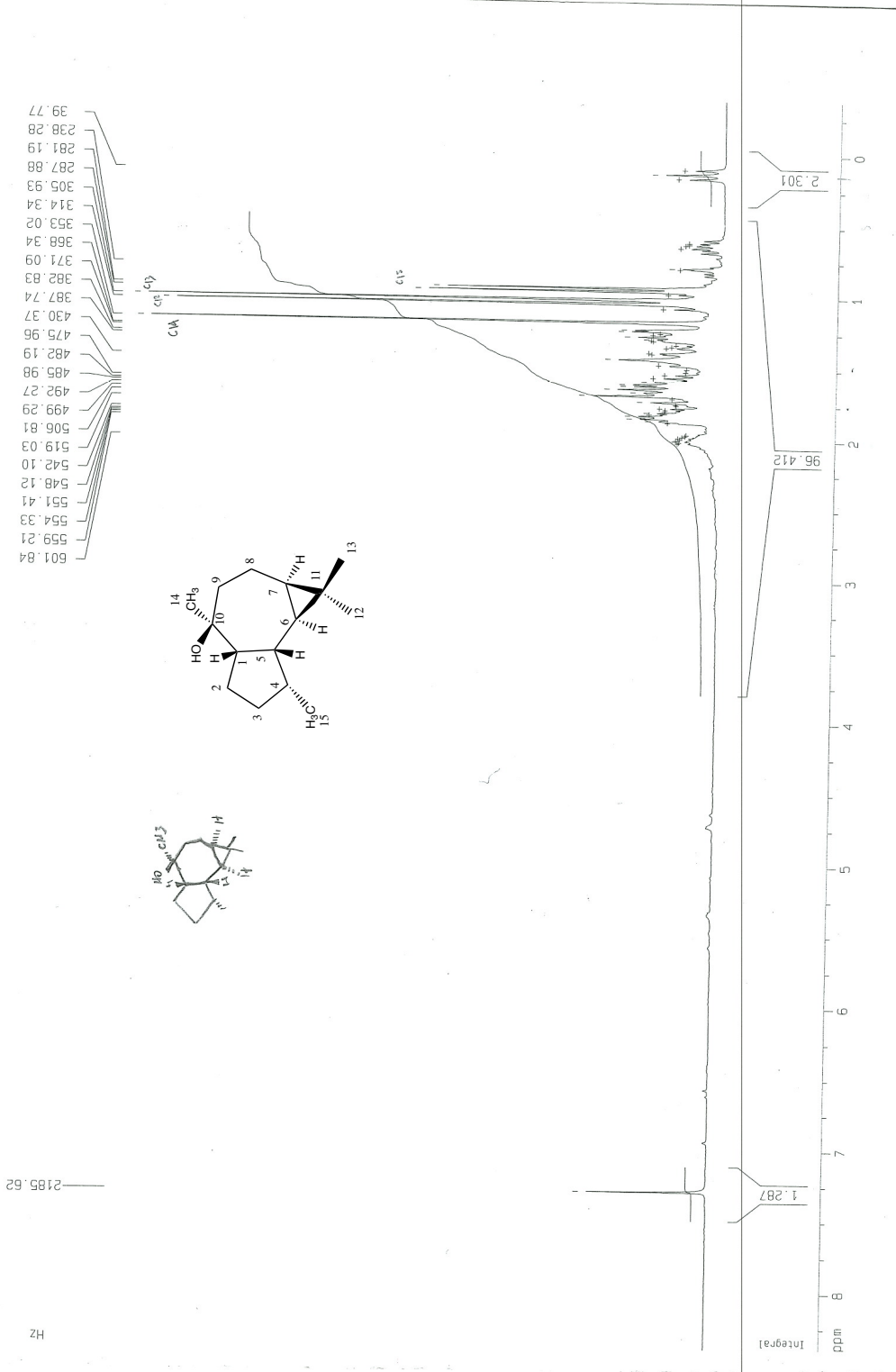


DEPT experiment (300 MHz) of oleanolic acid in CD₃OD.

JR31.1 70/33

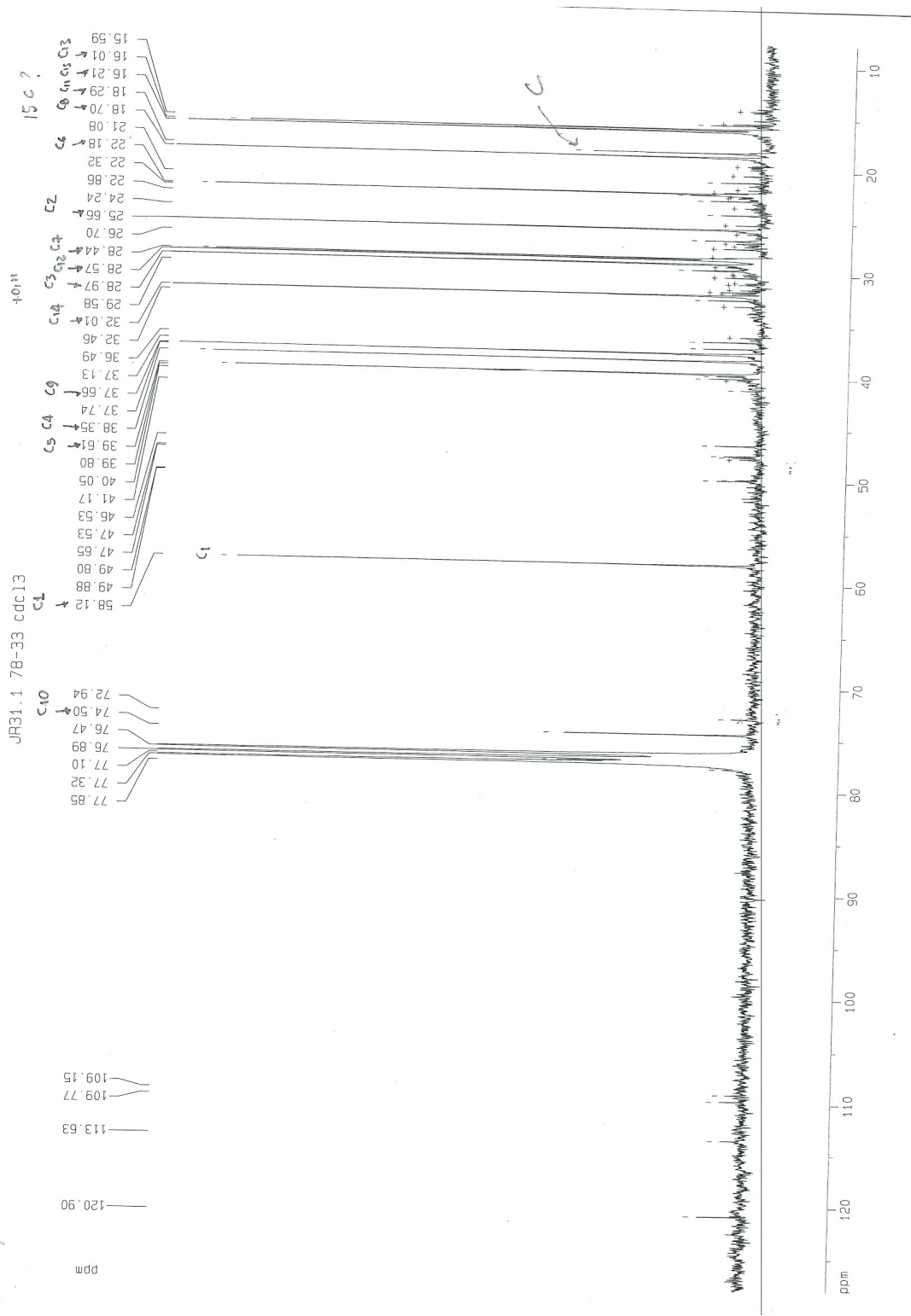
JR 31.1 78-33 cd13 aprile 8

416

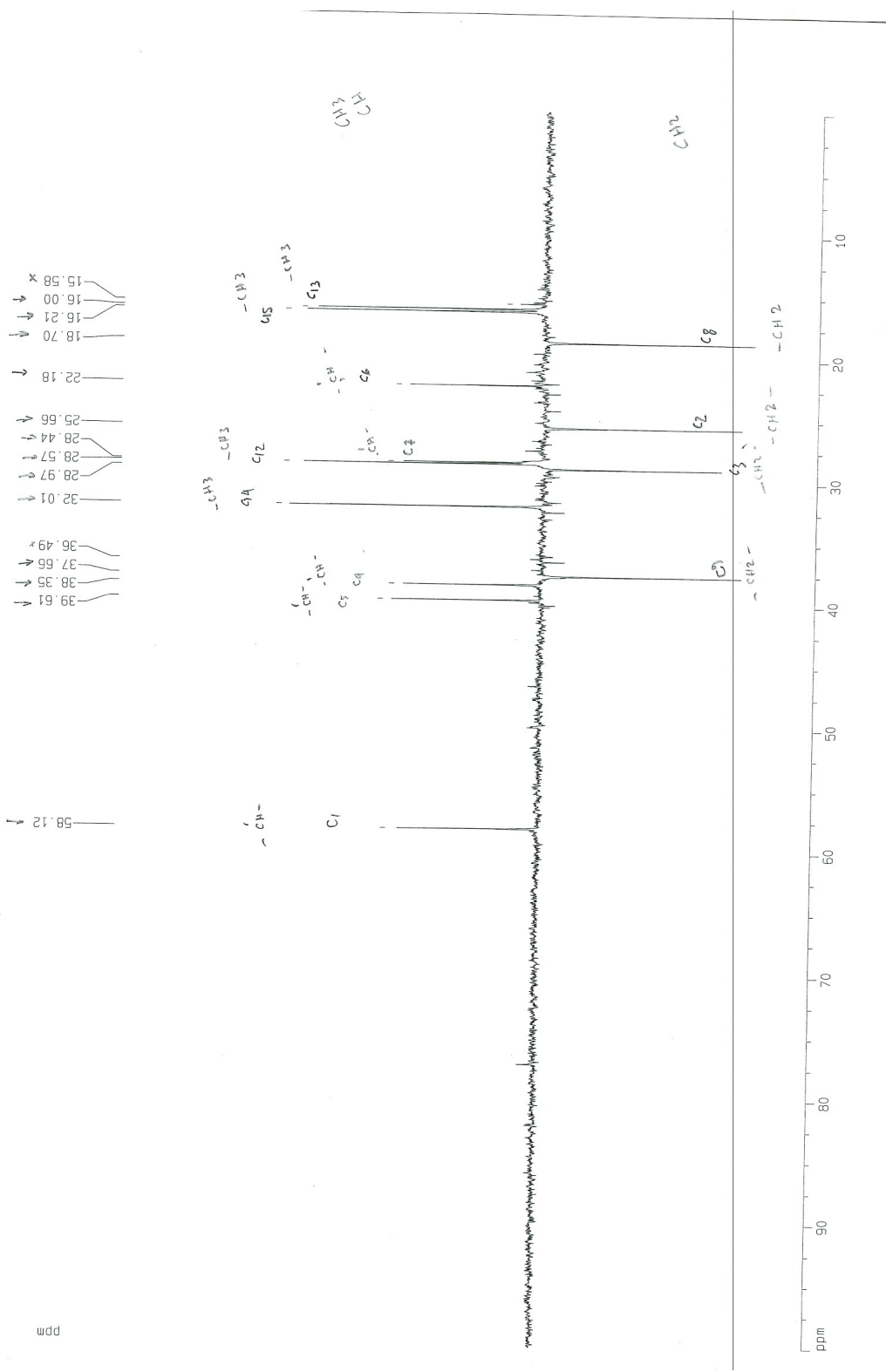


¹H-NMR of viridiflorol (CDCl₃, 300 MHz)

¹³C-NMR of viridiflorol (CDCl₃, 75 MHz)



JR 31.1 78-33 cdcl3

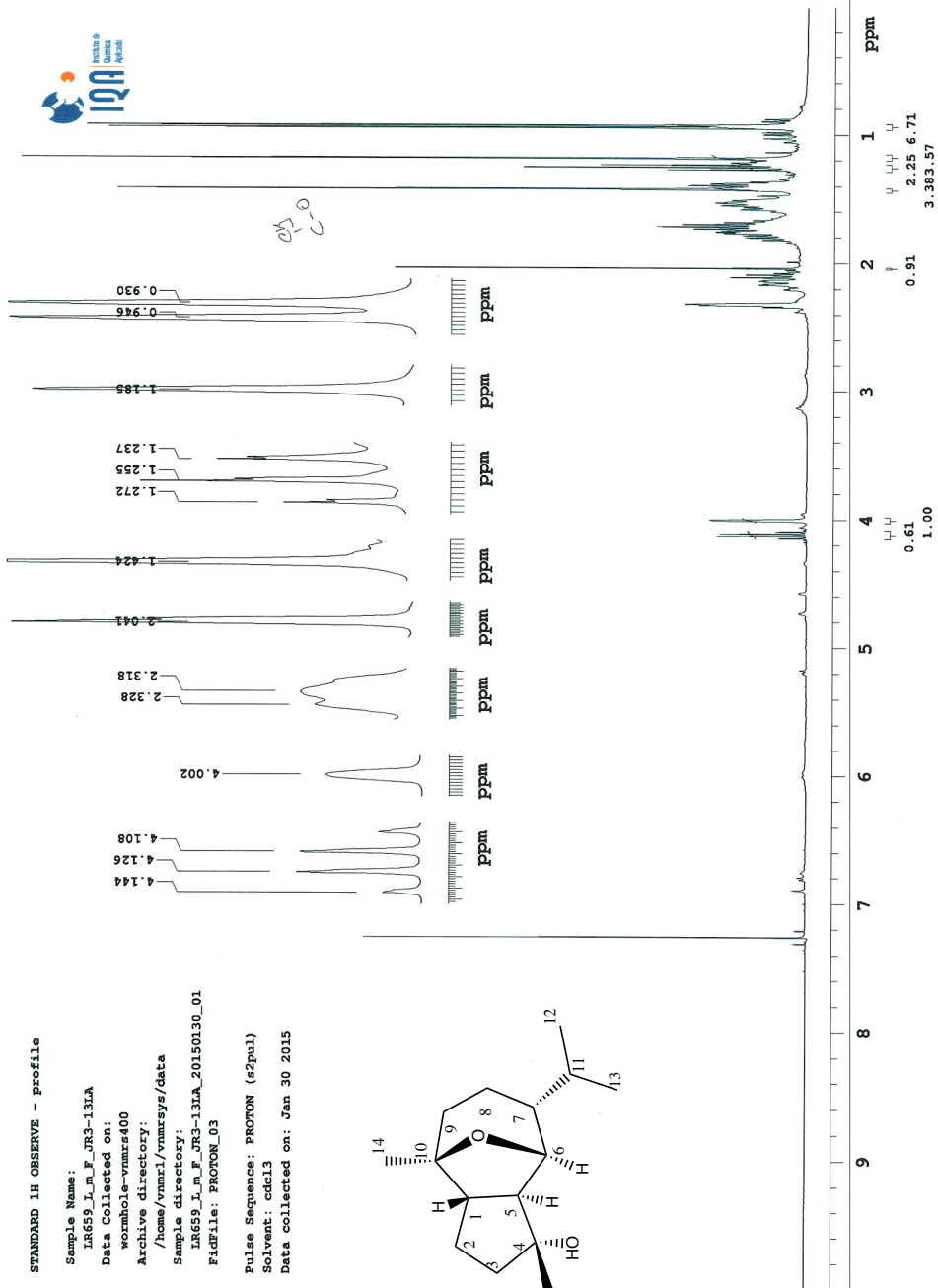
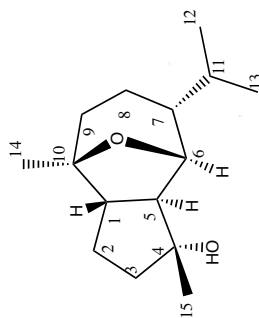


DEPT experiment (300 MHz) of viridiflorol in $CDCl_3$

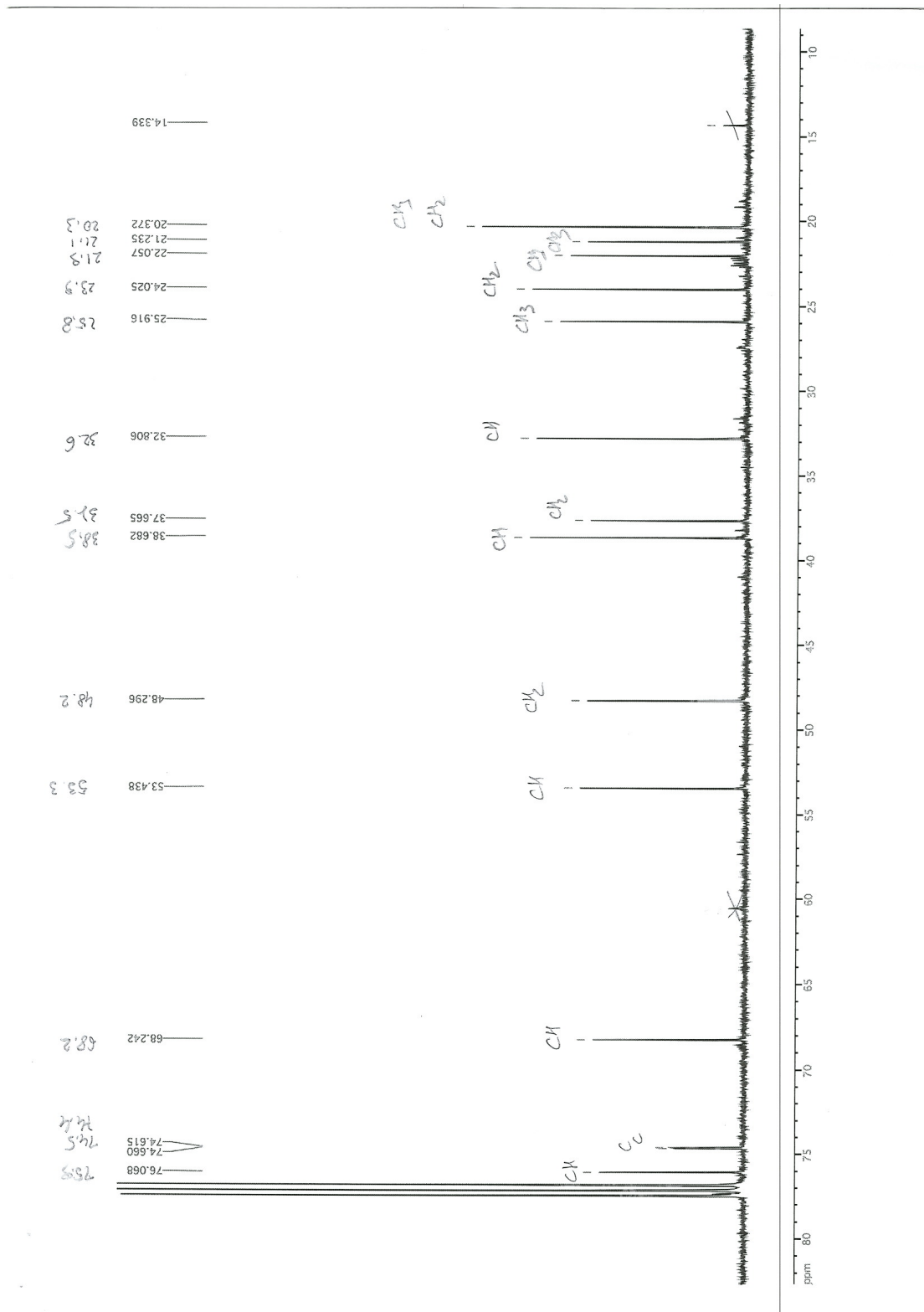
STANDARD 1H OBSERVE - profile

Sample Name:
IR659.L.m.F.JR3-13LA
Data Collected on:
wormhole-vnmrs600
Archive directory:
/home/vnmr1/vnmrsys/data
Sample directory:
IR659.L.m.F.JR3-13LA_20150130_01
FidFile: PROTON_03

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 30 2015



¹H-NMR of chrysothol (CDCl₃ 400 MHz)



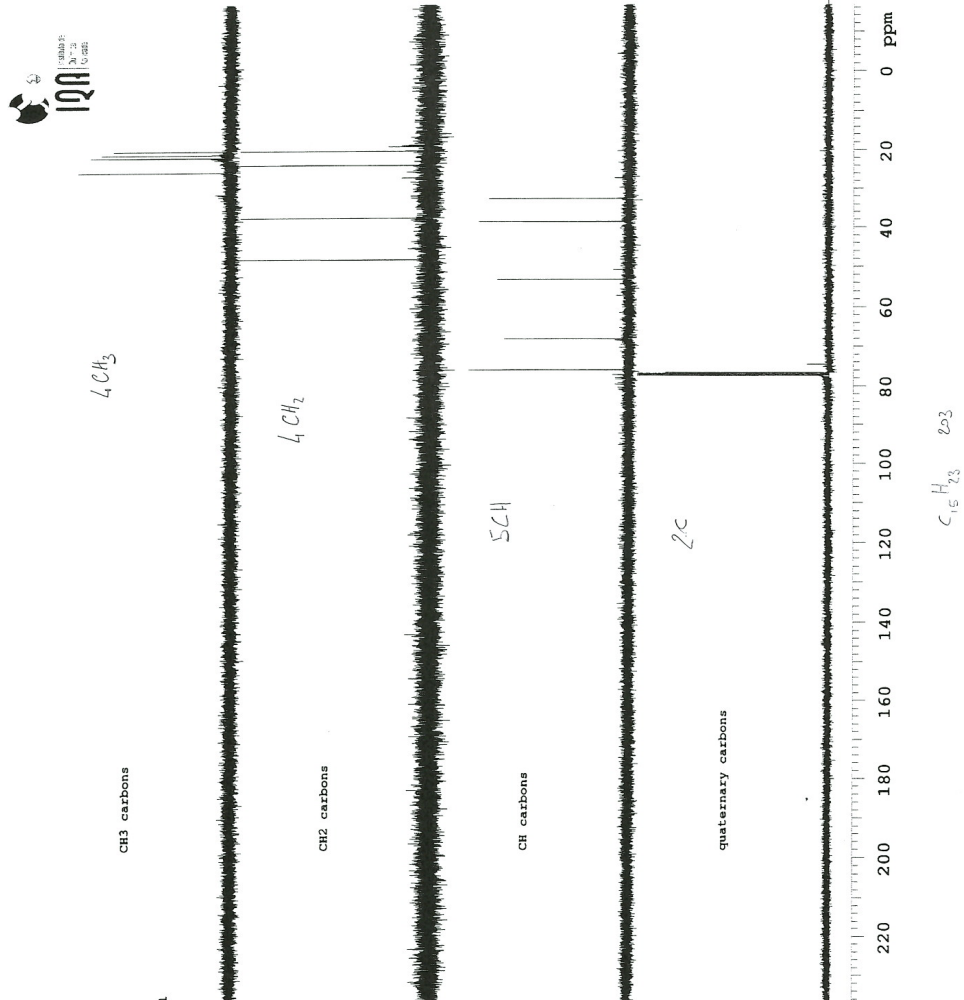
$^{13}\text{C-NMR}$ of chrysothol (CDCl_3 100 MHz)

STANDARD 1H OBSERVE - profile

Sample Name:
LR480_JR31_13-17
Data Collected on:
wormhole-vmrz400
Archive directory:
/home/vmrz1/vmrzsys/data
Sample directory:
LR480_JR31_13-17_20140828_01
File: DEPT_01

Pulse Sequence: DEPT
Solvent: cdcl3
Data collected on: Aug 28 2014

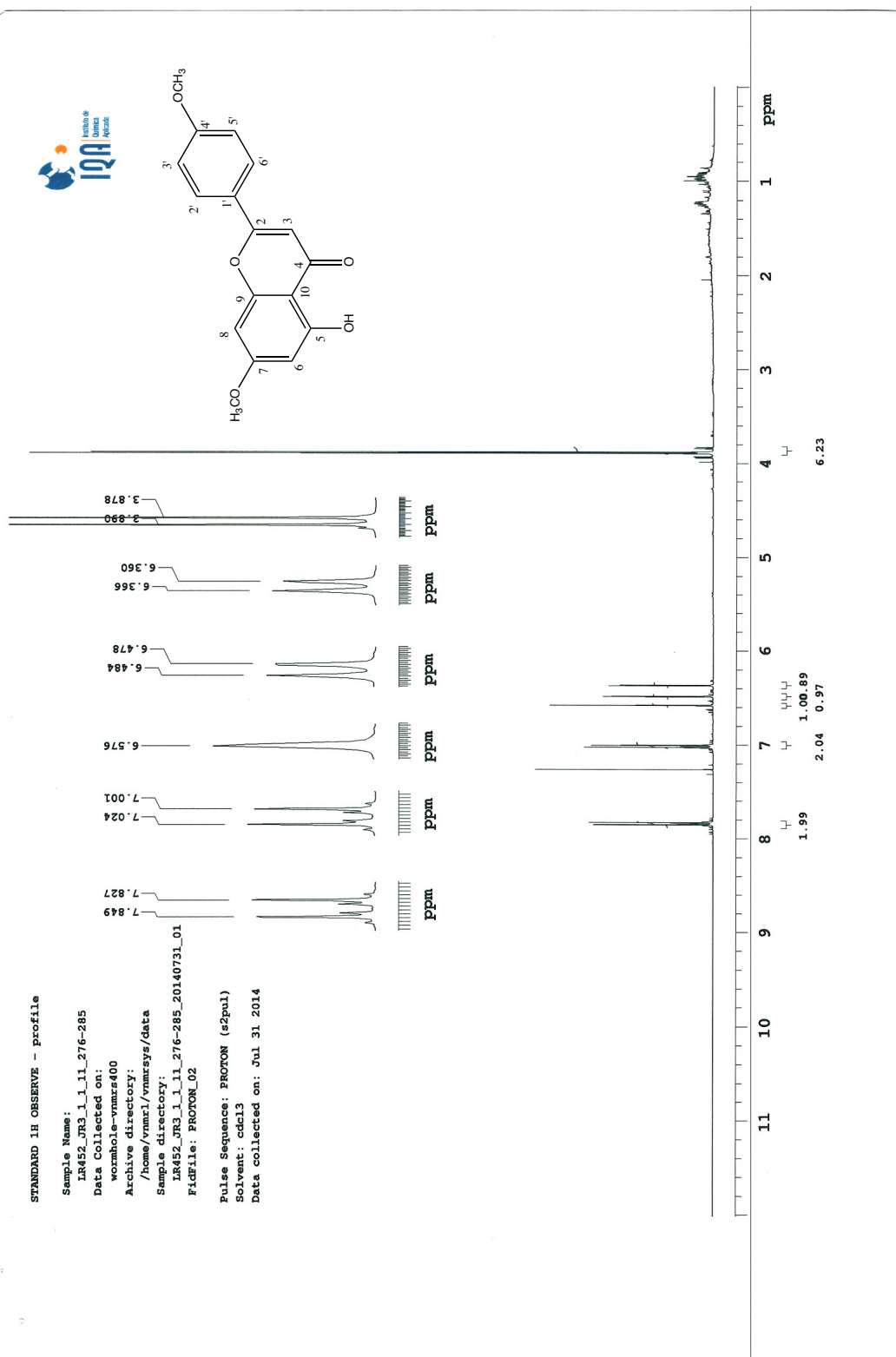
Temp: 25.0 C / 298.1 K
Operator: vmr1
Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
1024 repetitions
OBSERVE C13, 100.5376906 MHz
DECOUPLE H1, 399.8334195 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
Ft size 65536
Total time 7 hr, 30 min



$C_{15}H_{25}$
 $205 + 15 = 220$
 $220 + 18 = 238$
 $C_{15}H_{26}O_2$

DEPT experiment (400 MHz) of chrysothol in $CDCl_3$

¹H-NMR of 5-hydroxy-4',7-dimethoxy flavone (CDCl₃, 400 MHz)





STANDARD 1H OBSERVE - Profile

Sample Name: IR452_JR3_1_1_11_276-285
Data Collected on: wormhole-vnmrs400
Archive directory: /home/vnmr1/vnmrsys/data
Sample directory: IR452_JR3_1_1_11_276-285_20140731_01
FidFile: CARBON_01

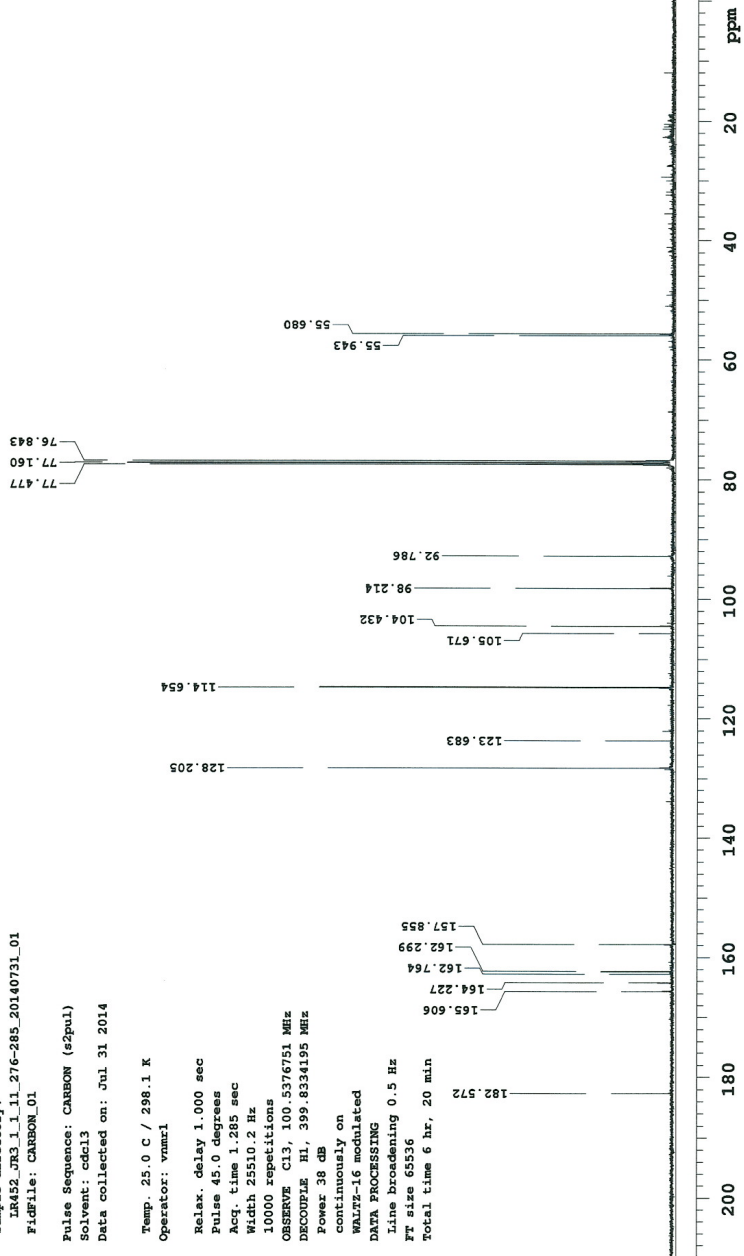
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jul 31 2014

Temp: 25.0 C / 298.1 K
Operator: vnmr1

Relax delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz

10000 repetitions
OBSERVE C13, 100.5376751 MHz
DECOUPLE H1, 399.8334195 MHz
Power 38 dB
continuously on

WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
Ff size 65536
Total time 6 hr, 20 min



¹³C-NMR of 5-hydroxy-4',7-dimethoxy flavone (CDCl₃, 100 MHz)



STANDARD 1H OBSERVE - profile

Sample Name:
IR452_JR3_1_1_11_276-285
Data Collected on:
wormhole-vnmrs400
Archive directory:
/home/vnmr1/vnmrsys/data
Sample directory:
IR452_JR3_1_1_11_276-285_20140731_01
FidFile: DEPT_01

CH3 carbons

Pulse Sequence: DEPT
Solvent: cdcl3
Data collected on: Aug 1 2014

Temp. 25.0 C / 298.1 K
Operator: vnmr1

CH2 carbons

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
1024 repetitions
OBSERVE C13, 100.5376906 MHz
DECOUPLE H1, 399.8334195 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
Ff size 65536
Total time 7 hr, 30 min

CH carbons

quaternary carbons

220 200 180 160 140 120 100 80 60 40 20 0 ppm

DEPT experiment (400 MHz) of 5-hydroxy-4',7-dimethoxy flavone in CDCl₃