# Total synthesis, structural elucidation and anti-inflammatory activity evaluation of 2-deoxy-3,6-anhydro hexofuranoside derivatives isolated from *Sauropus rostratus*

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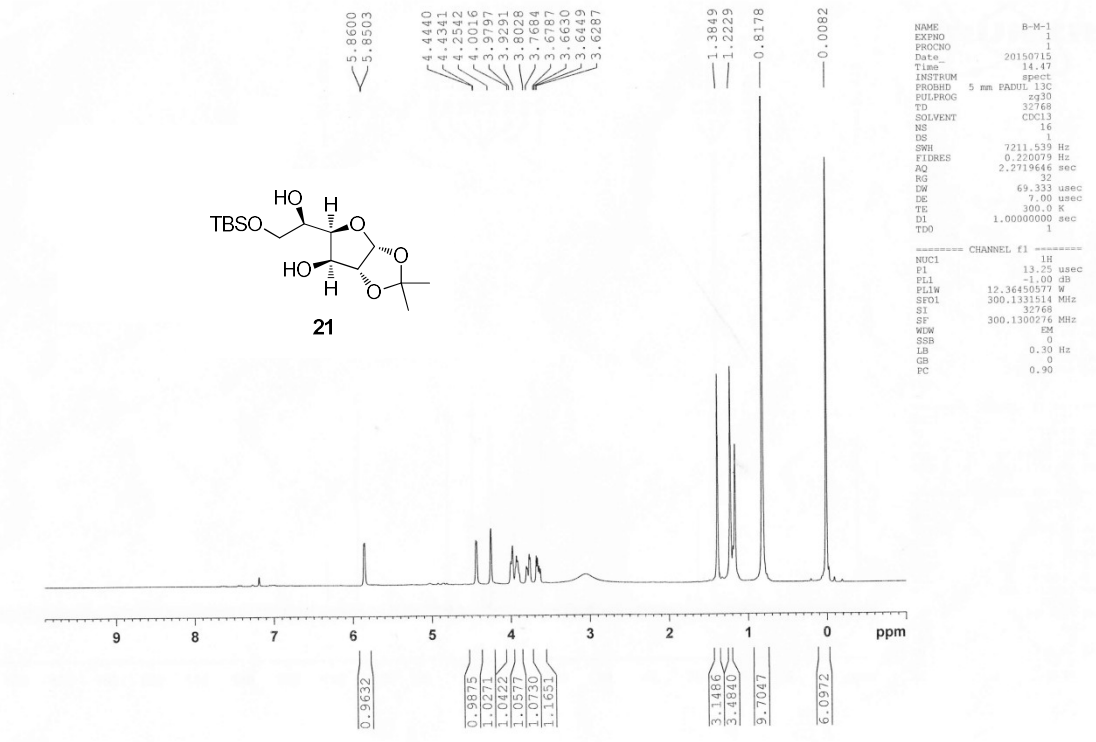
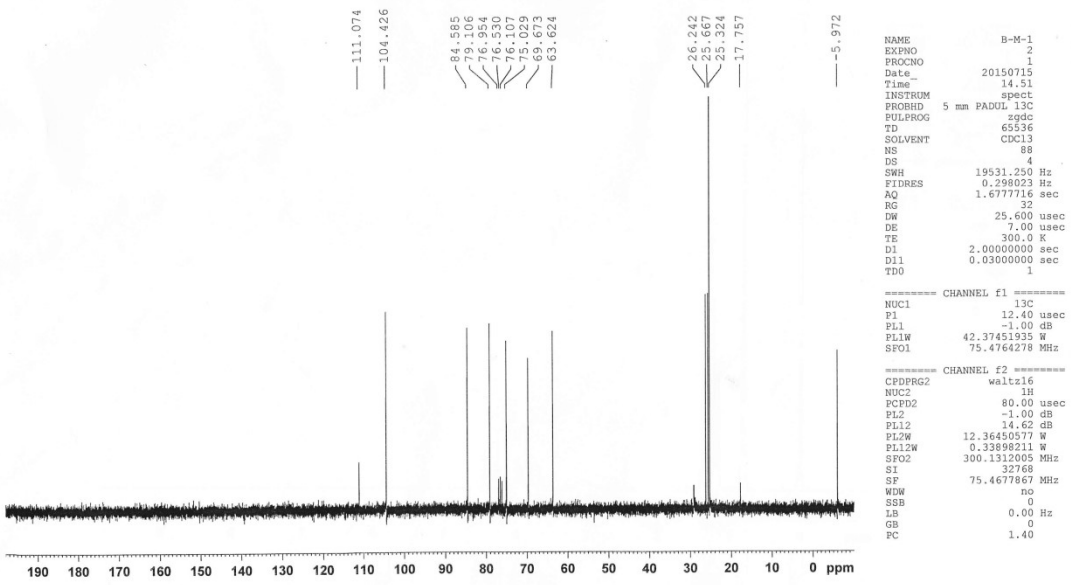
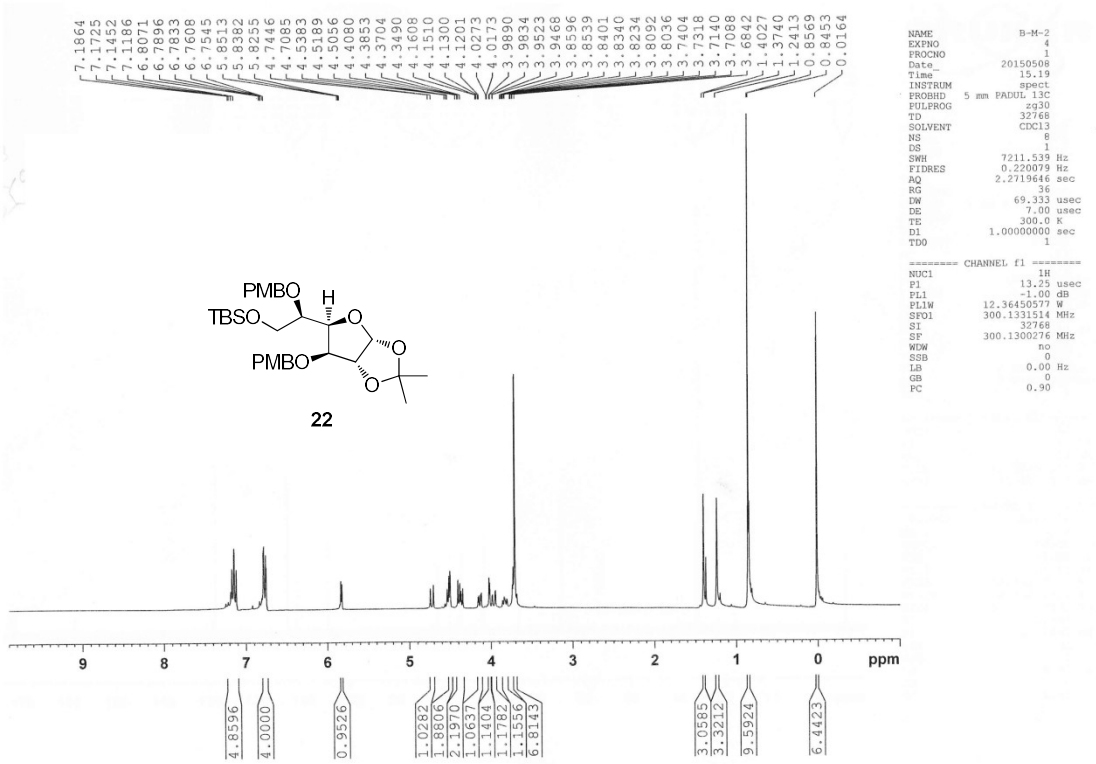
**CONTENTS:**

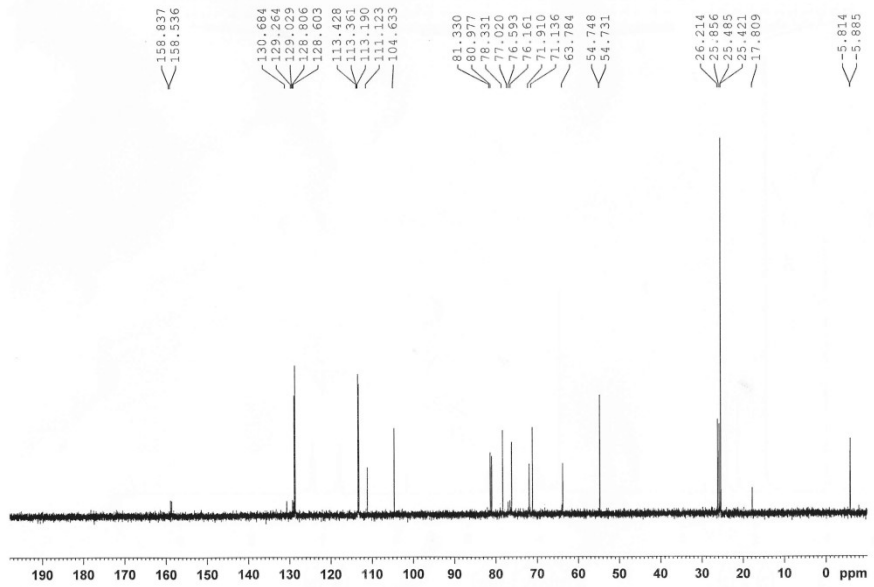
# 1. Copies of $^{1}H$ and $^{13}C$ NMR Spectra of New Compounds:






| | |
|---|---|
| NAME | B-M-2 |
| EXPNO | 4 |
| PROCNO | 1 |
| Date_ | 20150508 |
| Time | 15.19 |
| INSTRUM | spect |
| PROBHD | 5 mm PADUL 13C |
| PULPROG | zg30 |
| TD | 32768 |
| SOLVENT | CDCl3 |
| NS | 8 |
| DS | 1 |
| SWH | 7211.539 Hz |
| FIDRES | 0.220079 Hz |
| AQ | 2.2719646 sec |
| RG | 36 |
| DW | 69.333 usec |
| DE | 7.00 usec |
| TE | 300.0 K |
| D1 | 1.00000000 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| NUC1 | 1H |
| P1 | 13.25 usec |
| PL1 | -1.00 dB |
| PL1W | 12.36450577 W |
| SFO1 | 300.1331514 MHz |
| SI | 32768 |
| SF | 300.1300276 MHz |
| WDW | no |
| SSB | 0 |
| LB | 0.00 Hz |
| GB | 0 |
| PC | 0.90 |




| | |
|---|---|
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| PROCNO | 1 |
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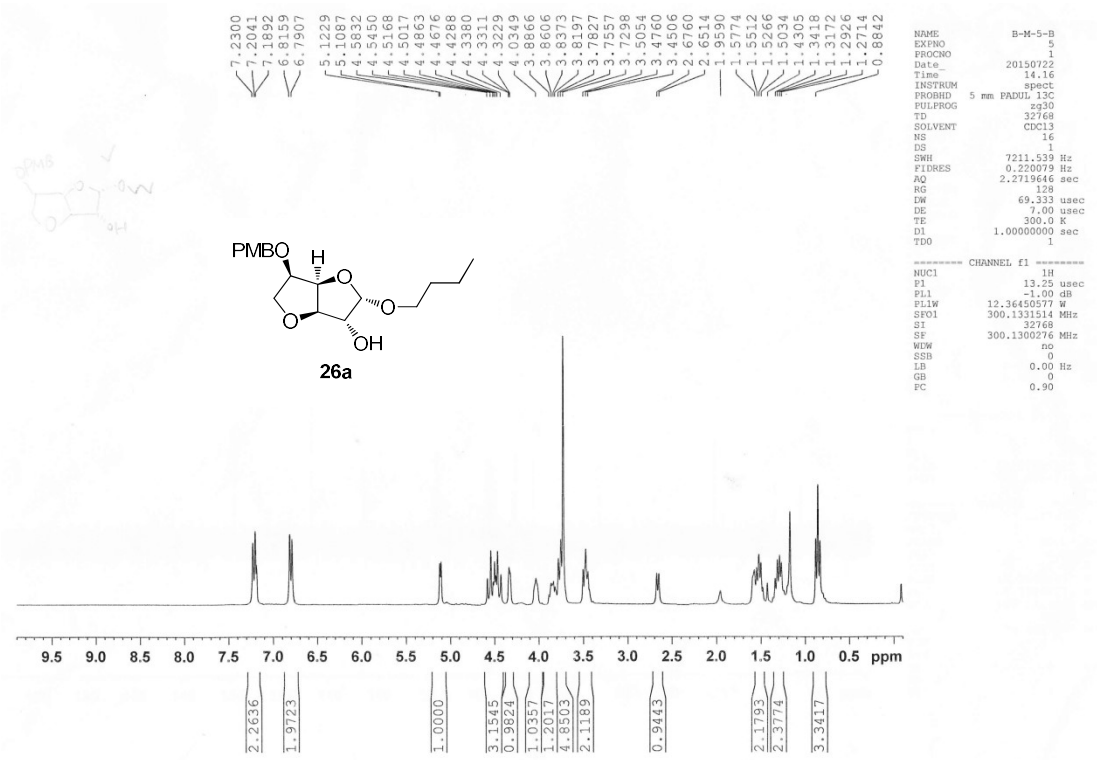
| Time | 15.23 |
| INSTRUM | spect |
| PROBHD | 5 mm PADUL 13C |
| PULPROG | zgdc |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 83 |
| DS | 4 |
| SWH | 19531.250 Hz |
| FIDRES | 0.298023 Hz |
| AQ | 1.6777716 sec |
| RG | 32 |
| DW | 25.600 usec |
| DE | 7.00 usec |
| TE | 300.0 K |
| D1 | 2.00000000 sec |
| D11 | 0.03000000 sec |
| TD0 | 1 |
| ======== CHANNEL f1 ======== | |
| NUC1 | 13C |
| P1 | 12.40 usec |
| PL1 | -1.00 dB |
| PL1W | 42.37451935 W |
| SFO1 | 75.4764278 MHz |
| ======== CHANNEL f2 ======== | |
| CPDPRG2 | waltz16 |
| NUC2 | 1H |
| PCPD2 | 80.00 usec |
| PL2 | -1.00 dB |
| PL12 | 14.62 dB |
| PL2W | 12.36450577 W |
| PL12W | 0.33898211 W |
| SFO2 | 300.1312005 MHz |
| SI | 32768 |
| SF | 75.4677867 MHz |
| WDW | no |
| SSB | 0 |
| LB | 0.00 Hz |
| GB | 0 |
| PC | 1.40 |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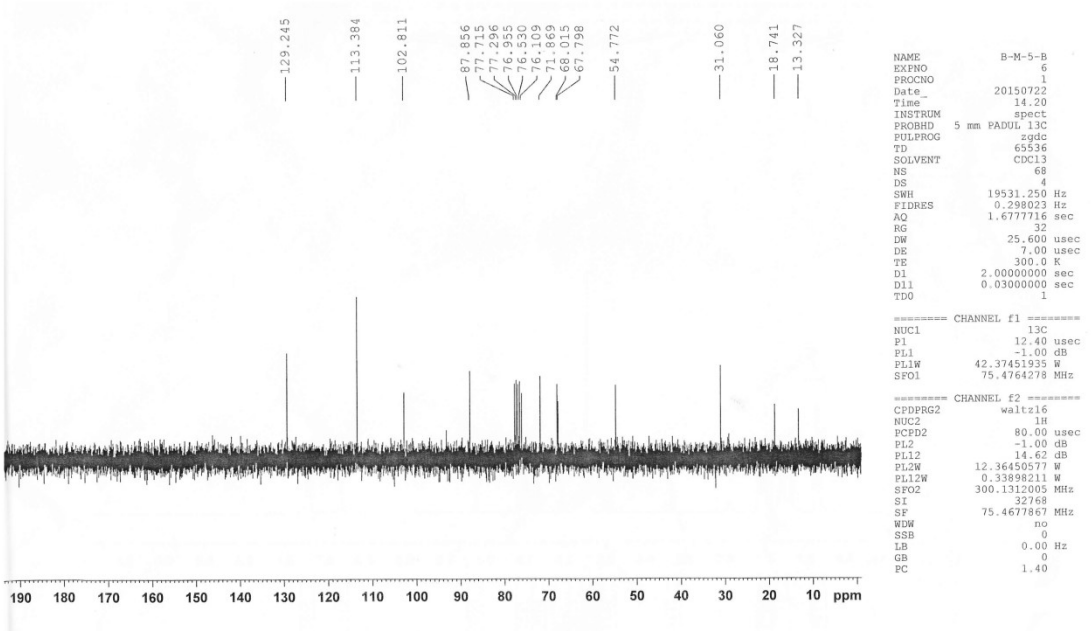
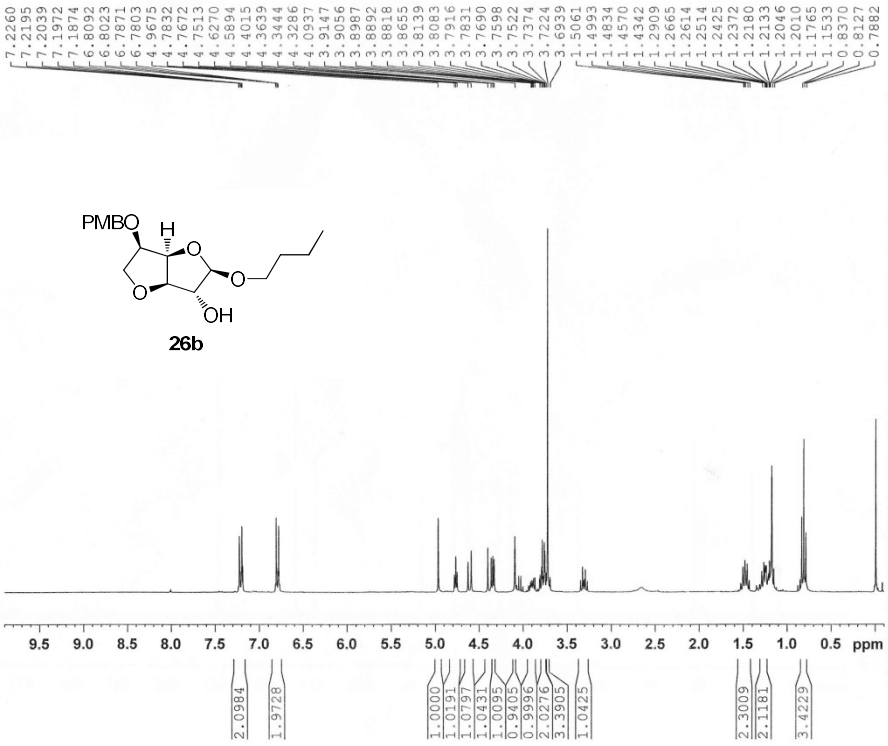
6.8159
6.7907
5.1229
5.1087
4.5832
4.5450
4.5168
4.5017
4.4863
4.4676
4.4288
4.3380
4.3311
4.3229
4.0349
3.8866
3.8606
3.8373
3.8197
3.7827
3.7557
3.7298
3.5054
3.4760
3.4506
2.6760
2.6514
1.9590
1.5774
1.5512
1.5266
1.5034
1.4305
1.3418
1.3172
1.2926
1.2714
0.8842
PMBO
H
O
O
O
OH
26a
NAME B-M-5-B
EXPNO 5
PROCNO 1
Date_ 20150722
Time 14.16
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 1
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719646 sec
RG 128
DW 69.333 usec
DE 7.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.25 usec
PL1 -1.00 dB
PL1W 12.36450577 W
SFO1 300.1331514 MHz
SI 32768
SF 300.1300276 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.2636
1.9723
1.0000
3.1545
0.9824
1.0357
1.2017
4.8503
2.1189
0.9443
2.1793
2.3774
3.3417


129.245
113.384
102.811
87.856
77.715
77.296
76.955
76.530
76.109
71.869
68.015
67.798
54.772
31.060
18.741
13.327
NAME B-M-5-B
EXPNO 6
PROCNO 1
Date_ 20150722
Time 14.20
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 68
DS 4
SWH 19531.250 Hz
FIDRES 0.298023 Hz
AQ 1.6777716 sec
RG 32
DW 25.600 usec
DE 7.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.40 usec
PL1 -1.00 dB
PL1W 42.37451935 W
SFO1 75.4764278 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.62 dB
PL2W 12.36450577 W
PL12W 0.33898211 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677867 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

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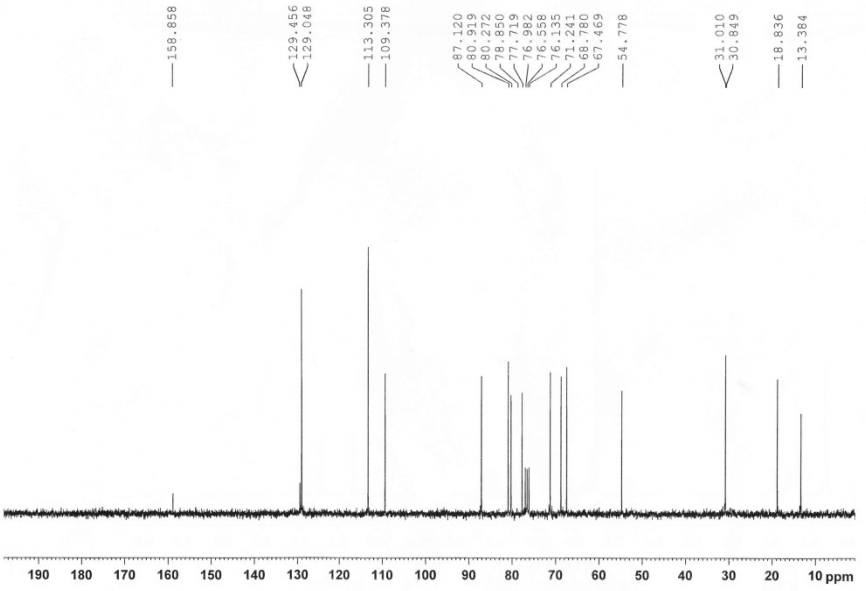
EXPNO                  10
PROCNO                  1
Date_            20150730
Time                12.44
INSTRUM             spect
PROBHD   5 mm PADUL 13C
PULPROG              zg30
TD                  32768
SOLVENT             CDC13
NS                     16
DS                      1
SWH            7211.539 Hz
FIDRES         0.220079 Hz
AQ             2.2719646 sec
RG                     57
DW                69.333 usec
DE                 7.00 usec
TE                300.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.25 usec
PL1                -1.00 dB
PL1W          12.36450577 W
SFO1          300.1331514 MHz
SI                  32768
SF            300.1300276 MHz
WDW                    no
SSB                     0
LB                 0.00 Hz
GB                      0
PC                   0.90
```

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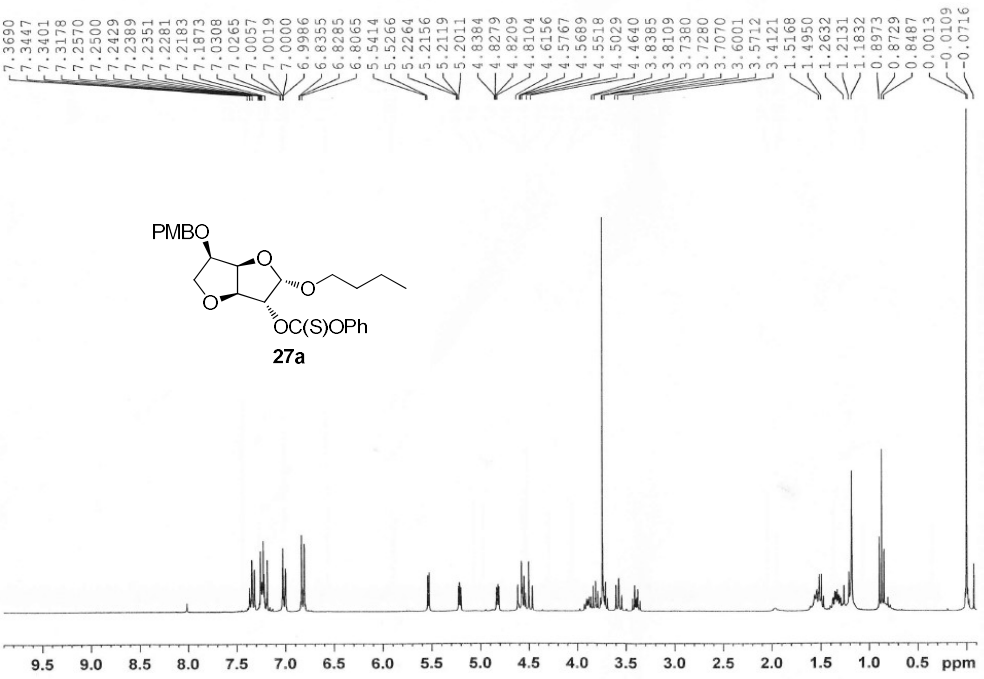
NAME              B-M-5-A
EXPNO                  11
PROCNO                  1
Date_            20150730
Time                12.49
INSTRUM             spect
PROBHD   5 mm PADUL 13C
PULPROG             zgdc
TD                  65536
SOLVENT             CDC13
NS                     92
DS                      4
SWH           19531.250 Hz
FIDRES         0.298023 Hz
AQ             1.6777716 sec
RG                     32
DW                25.600 usec
DE                 7.00 usec
TE                300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 12.40 usec
PL1                -1.00 dB
PL1W          42.37451935 W
SFO1           75.4764278 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               14.62 dB
PL2W          12.36450577 W
PL12W          0.33898211 W
SFO2          300.1312005 MHz
SI                  32768
SF             75.4677867 MHz
WDW                   EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                   1.40
```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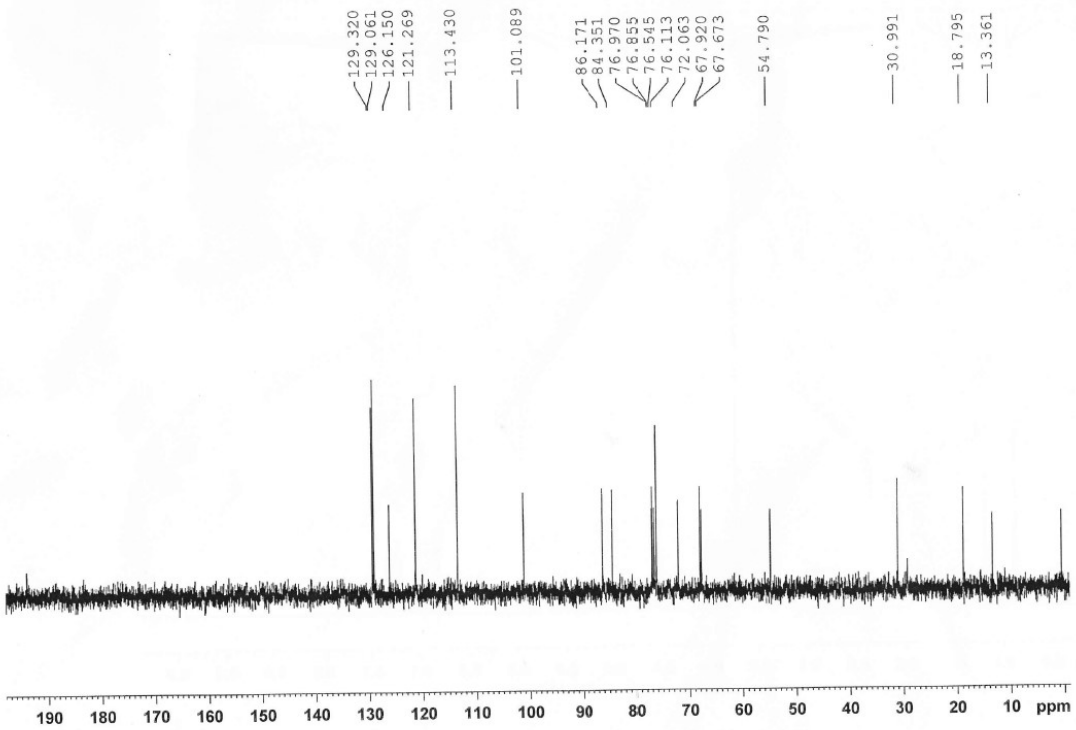
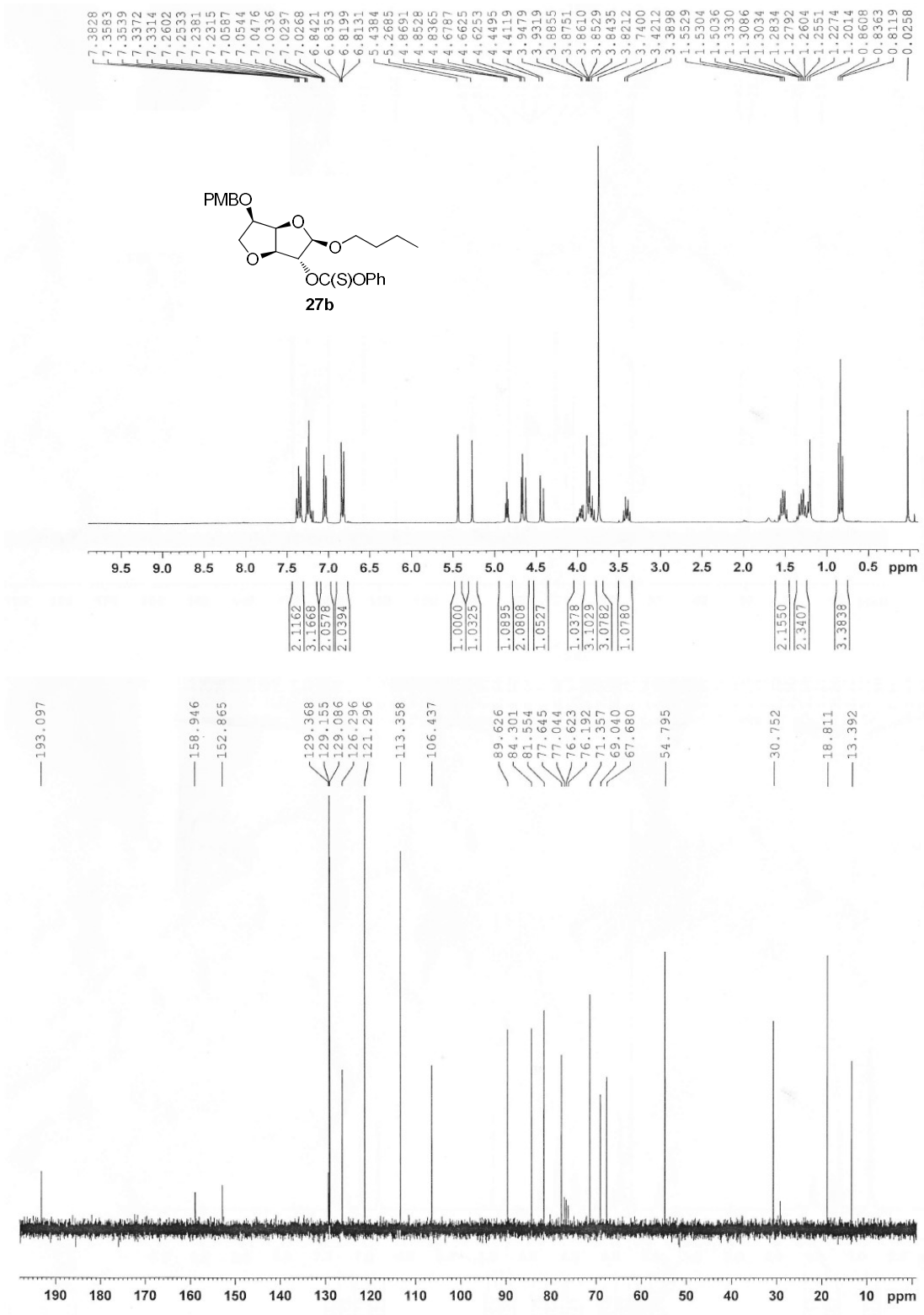
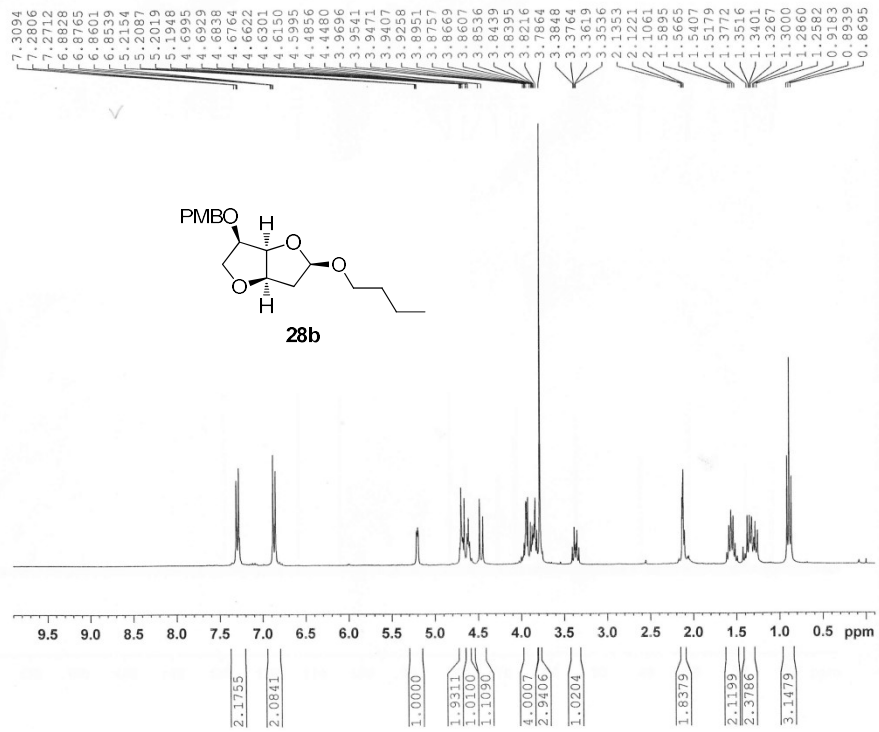
7.3178
7.2570
7.2500
7.2429
7.2389
7.2351
7.2281
7.2183
7.1873
7.0308
7.0265
7.0057
7.0019
7.0000
6.9986
6.8355
6.8285
6.8065
5.5414
5.5266
5.2264
5.2156
5.2119
5.2011
4.8384
4.8279
4.8209
4.8104
4.6156
4.5767
4.5689
4.5518
4.5029
4.4640
3.8385
3.8109
3.7380
3.7280
3.7070
3.6001
3.5712
3.4121
1.5168
1.4950
1.2632
1.2131
1.1832
0.8973
0.8729
0.8487
0.0013
-0.0109
-0.0716
PMBO
O
O
O
OC(S)OPh
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

**27a**


129.320
129.061
126.150
121.269
113.430
101.089
86.171
84.351
76.970
76.855
76.545
76.113
72.063
67.920
67.673
54.790
30.991
18.795
13.361
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


PMBO
O
O
O
OC(S)OPh
27b
ppm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7.2712
6.8828
6.8765
6.8601
6.8539
5.2154
5.2087
5.2019
5.1948
4.6995
4.6929
4.6838
4.6764
4.6622
4.6301
4.6150
4.5995
4.4856
4.4480
3.9696
3.9541
3.9471
3.9407
3.8958
3.8951
3.8757
3.8669
3.8607
3.8536
3.8439
3.8395
3.8216
3.7864
3.7764
3.3848
3.3764
3.3619
3.3536
2.1353
2.1221
2.1061
1.5895
1.5665
1.5407
1.5179
1.3772
1.3516
1.3401
1.3267
1.3000
1.2860
1.2582
0.9183
0.8939
0.8695
PMBO
H
O
O
O
H
28b
NAME LLY-5-1
EXPNO 3
PROCNO 1
Date_ 20150508
Time 16.13
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 1
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719646 sec
RG 20.2
DW 69.333 usec
DE 7.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.25 usec
PL1 -1.00 dB
PL1W 12.36450577 W
SFO1 300.1331514 MHz
SI 32768
SF 300.1300020 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.1755
2.0841
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1.0204
1.8379
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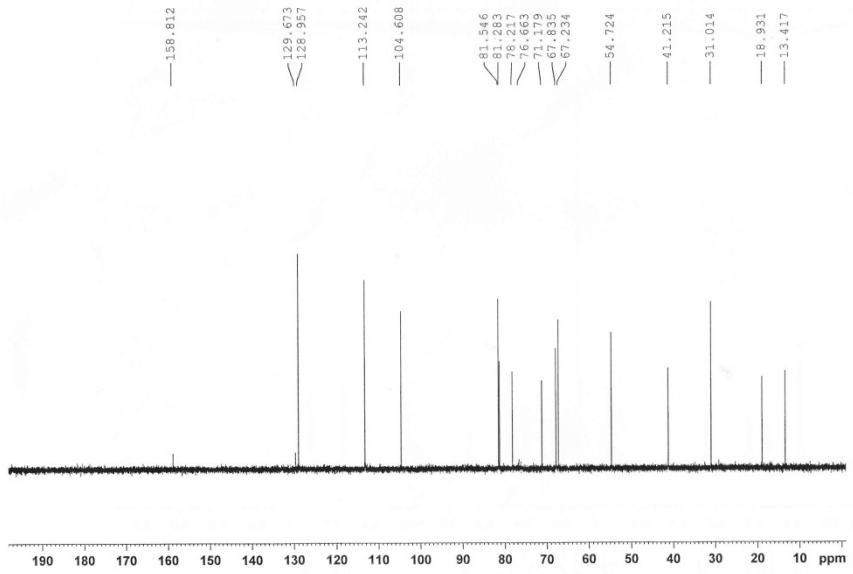
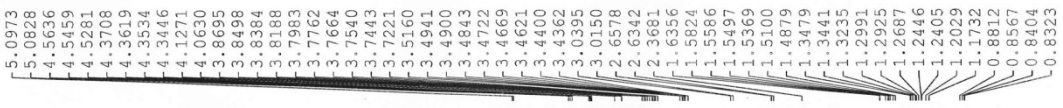
2.3766
3.1479


158.812
129.673
128.957
113.242
104.608
81.546
81.283
78.267
76.663
75.179
71.835
67.234
54.724
41.215
31.014
18.931
13.417
NAME LLY-5-1
EXPNO 4
PROCNO 1
Date_ 20150508
Time 16.16
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 37
DS 4
SWH 19531.250 Hz
FIDRES 0.298023 Hz
AQ 1.6777716 sec
RG 32
DW 25.600 usec
DE 7.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.40 usec
PL1 -1.00 dB
PL1W 42.37451935 W
SFO1 75.4764278 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.62 dB
PL2W 12.36450577 W
PL12W 0.33898211 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677867 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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5.0828
4.5636
4.5459
4.5281
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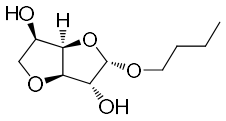
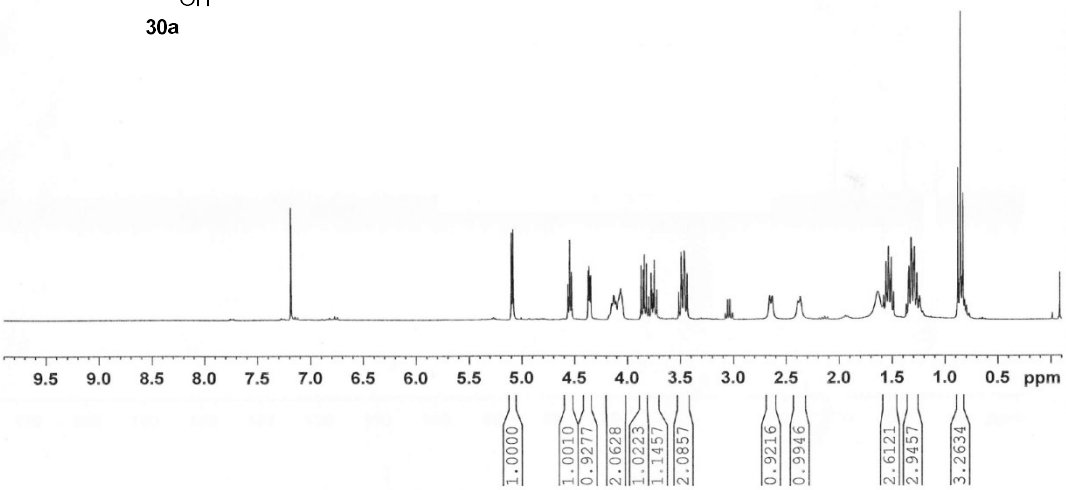
4.3619
4.3534
4.3446
4.1271
4.0630
3.8695
3.8498
3.8384
3.8188
3.7983
3.7762
3.7664
3.7540
3.7443
3.7221
3.5160
3.4941
3.4900
3.4843
3.4722
3.4669
3.4621
3.4400
3.4362
3.0395
3.0150
2.6578
2.6342
2.3681
1.6356
1.5824
1.5586
1.5497
1.5369
1.5100
1.4879
1.3479
1.3441
1.3235
1.2991
1.2925
1.2687
1.2446
1.2405
1.2029
1.1732
0.8812
0.8567
0.8404
0.8323


HO
H
O
O
O
OH

**30a**


9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.0000
1.0010
0.9277
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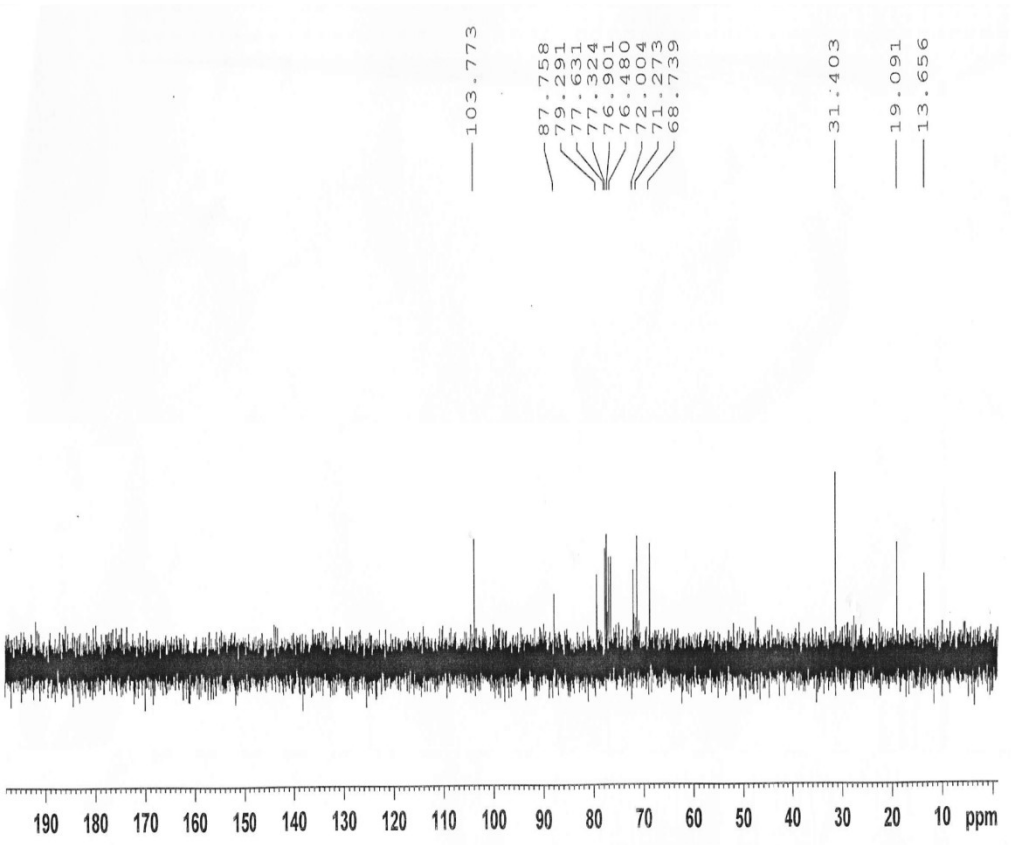
1.0223
1.1457
2.0857
0.9216
0.9946
2.6121
2.9457
3.2634


103.773
87.758
79.291
77.631
77.324
76.901
76.480
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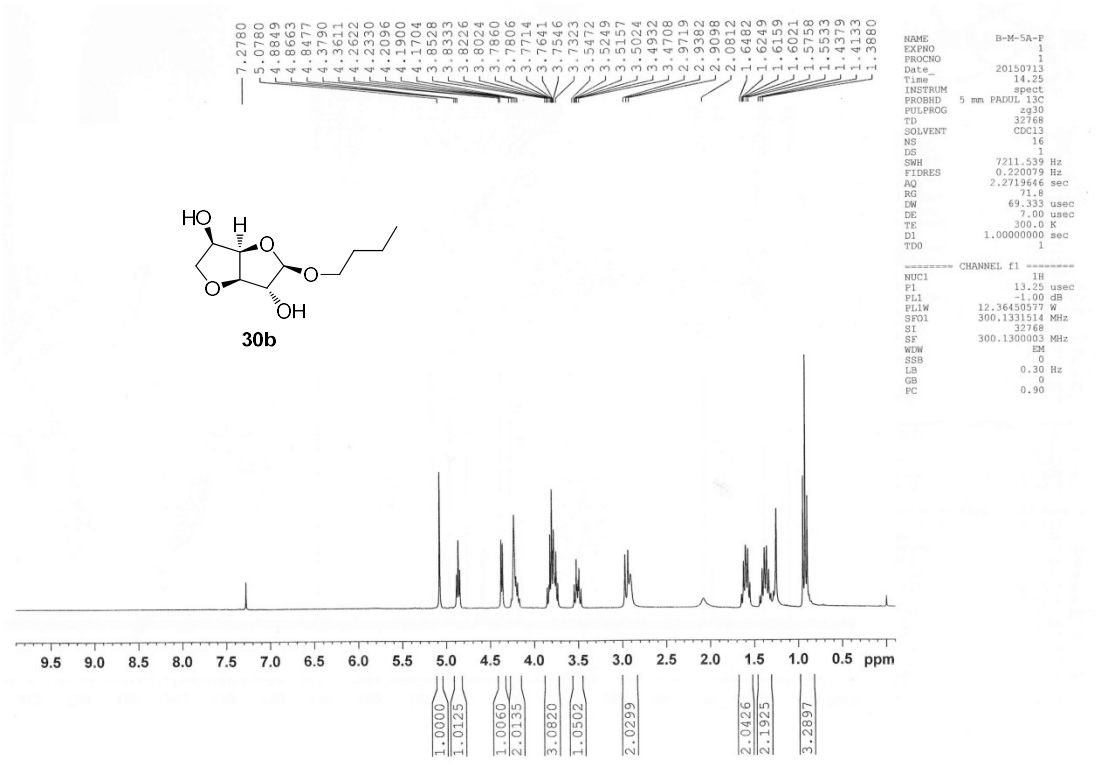
71.273
68.739
31.403
19.091
13.656
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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4.8663
4.8477
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4.3611
4.2622
4.2330
4.2096
4.1900
4.1704
3.8528
3.8333
3.8226
3.8024
3.7860
3.7806
3.7714
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3.7323
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3.5024
3.4932
3.4708
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HO
H
O
O
O
OH
30b
NAME B-M-5A-P
EXPNO 1
PROCNO 1
Date_ 20150713
Time 14.25
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 1
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719646 sec
RG 71.8
DW 69.333 usec
DE 7.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.25 usec
PL1 -1.00 dB
PL1W 12.36450577 W
SFO1 300.1331514 MHz
SI 32768
SF 300.1300003 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.0000
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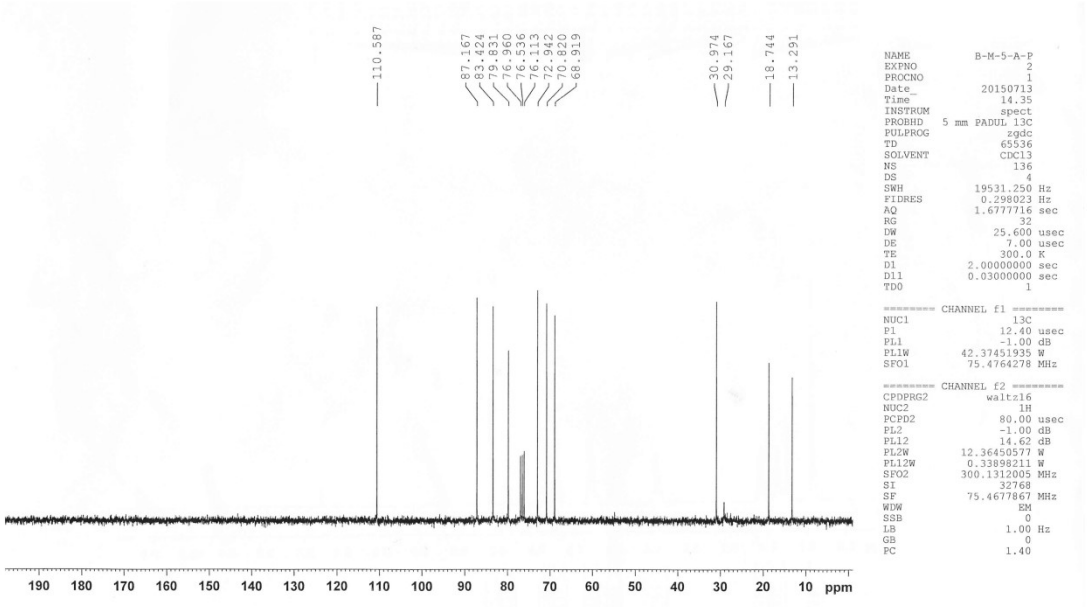
1.0502
2.0299
2.0426
2.1925
3.2897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29.167
18.744
13.291
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PROCNO 1
Date_ 20150713
Time 14.35
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 136
DS 4
SWH 19531.250 Hz
FIDRES 0.298023 Hz
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RG 32
DW 25.600 usec
DE 7.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
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P1 12.40 usec
PL1 -1.00 dB
PL1W 42.37451935 W
SFO1 75.4764278 MHz
======== CHANNEL f2 ========
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NUC2 1H
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PL2 -1.00 dB
PL12 14.62 dB
PL2W 12.36450577 W
PL12W 0.33898211 W
SFO2 300.1312005 MHz
SI 32768
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WDW EM
SSB 0
LB 1.00 Hz
GB 0
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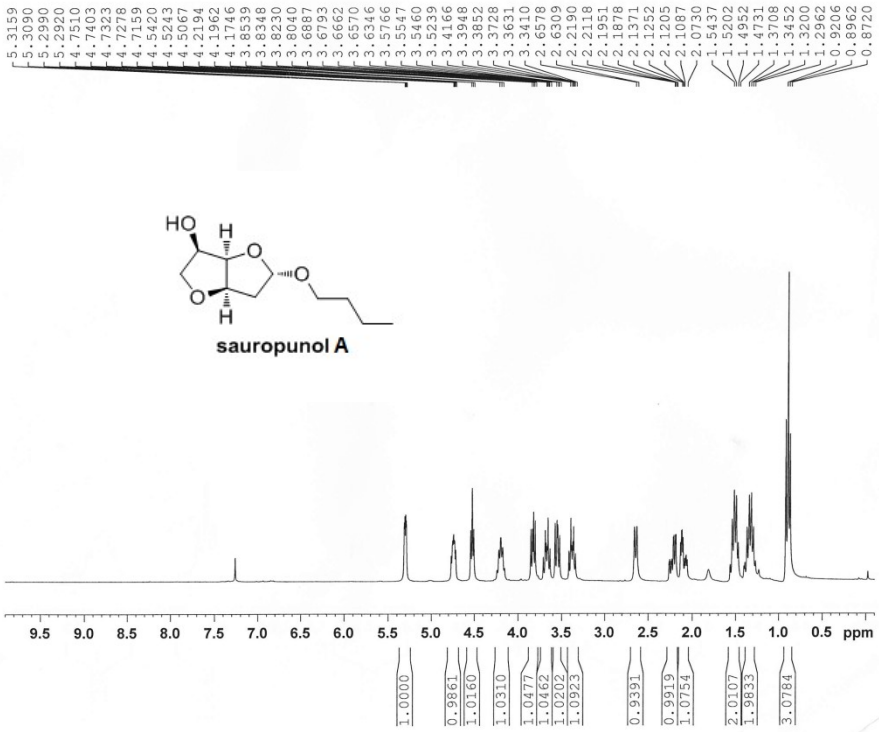





sauropunol A

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PROCNO                    1
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TE                300.0 K
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TD0                       1

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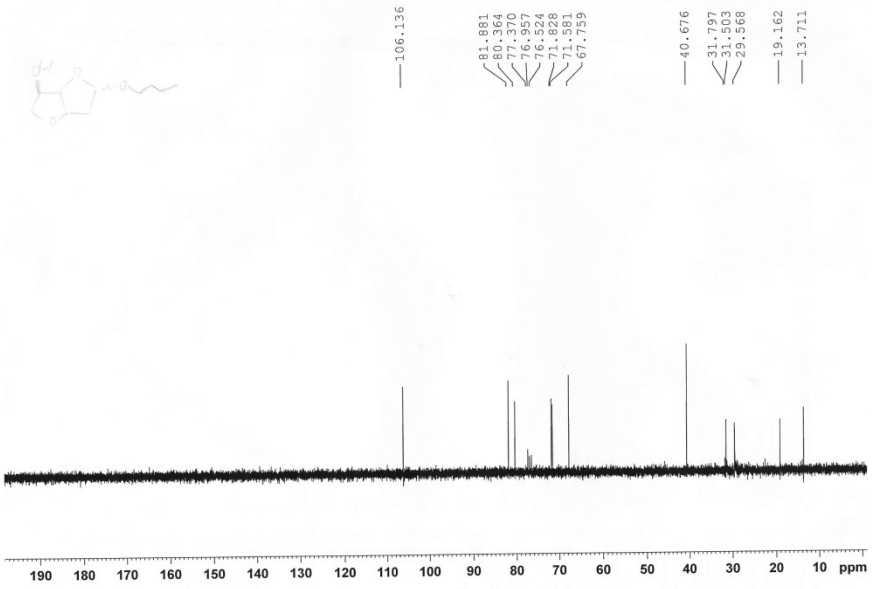


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NS                       31
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FIDRES           0.298023 Hz
AQ               1.6777716 sec
RG                       32
DW                25.600 usec
DE                 7.00 usec
TE                300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
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PL1                  -1.00 dB
PL1W            42.37451935 W
SFO1           75.4764278 MHz

======== CHANNEL f2 ========
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NUC2                     1H
PCPD2                80.00 usec
PL2                  -1.00 dB
PL12                 14.62 dB
PL2W            12.36450577 W
PL12W            0.33898211 W
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SI                    32768
SF             75.4677573 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.40
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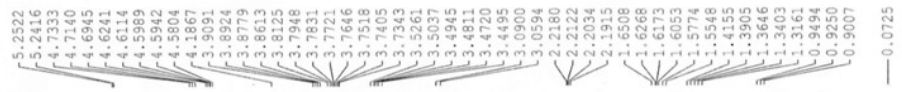
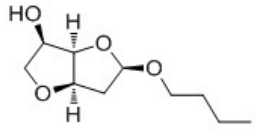
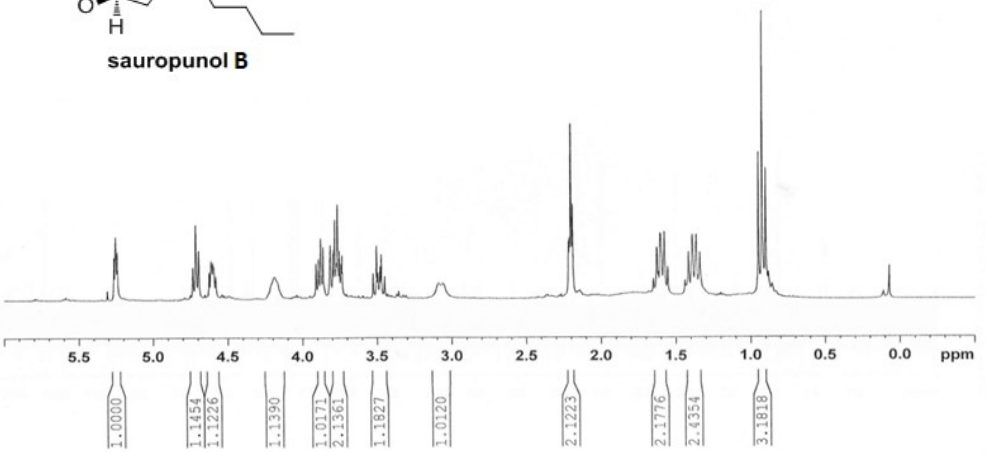
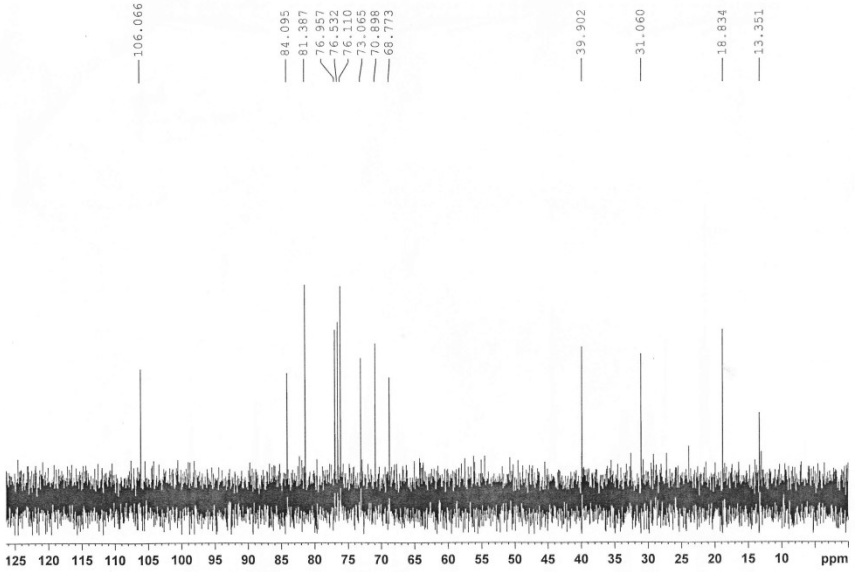



**sauropunol B**

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PROCNO                    1
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TD                   65536
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DS                       4
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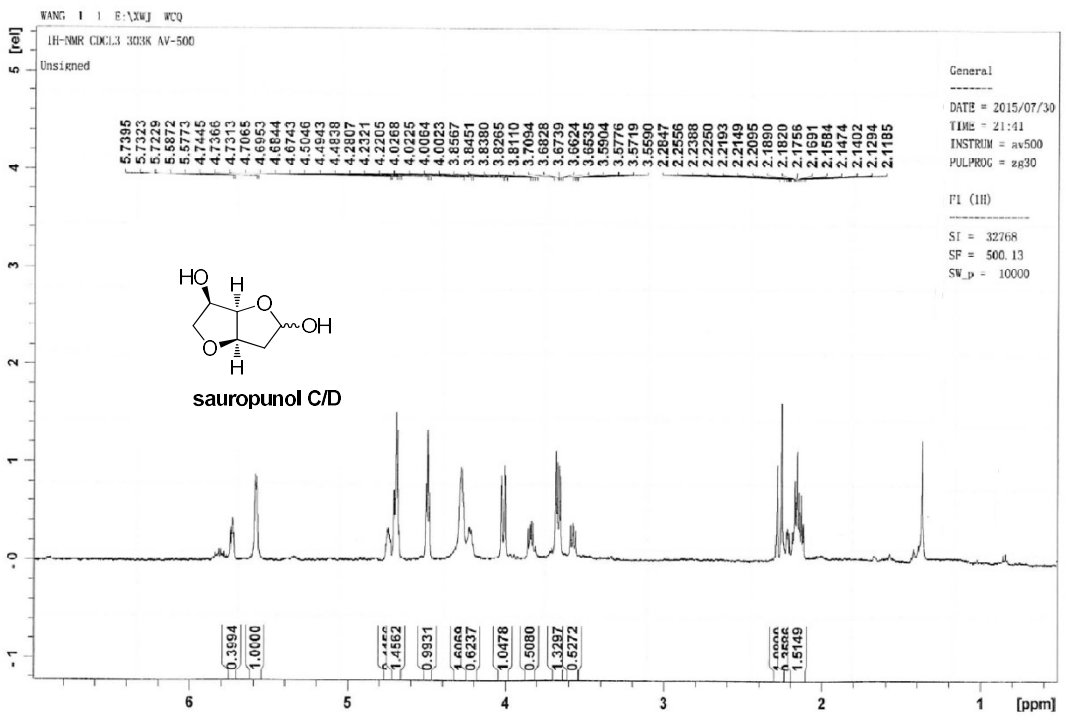
FIDRES               0.298023 Hz
AQ                1.6777716 sec
RG                      32
DW                   25.600 usec
DE                    7.00 usec
TE                   300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    13C
P1                    12.40 usec
PL1                   -1.00 dB
PL1W            42.37451935 W
SFO1             75.4764278 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2                 80.00 usec
PL2                   -1.00 dB
PL12                  14.62 dB
PL2W            12.36450577 W
PL12W            0.33898211 W
SFO2            300.1312005 MHz
SI                   32768
SF               75.4677867 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.40
```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General
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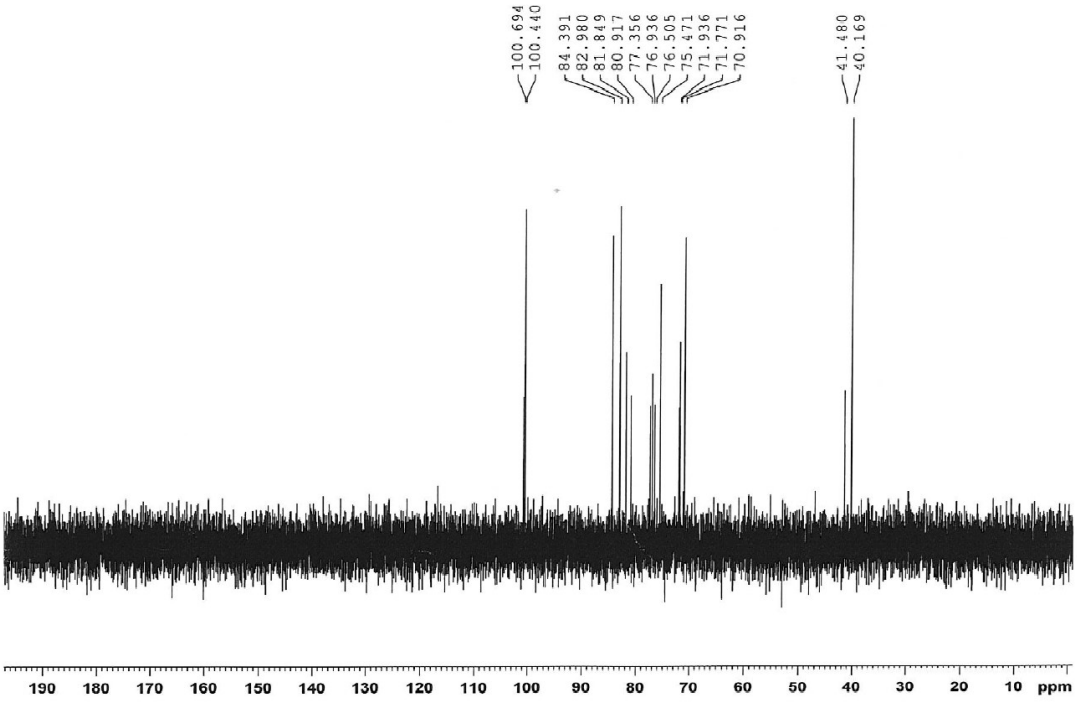
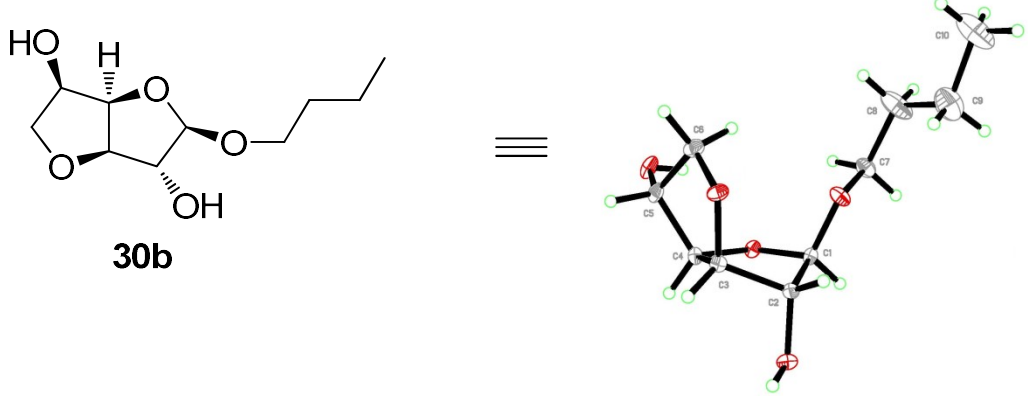
[rel]
[ppm]


ppm

## 2. X-ray Structural Analysis of 30b




# Crystal Data

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|---|---|
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| _chemical_formula_weight | 218.24 |
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| _symmetry_space_group_name_H-M | 'P2(1)2(1)2(1) ' |
| _cell_length_a/b/c [Angstrom] | 5.3124(4)/7.0459(8)/29.215(2) |
| _cell_angle_alpha/beta/gamma[deg] | 90.00/90.00/90.00 |
| _cell_volume | 1093.53(17) |
| _cell_formula_units_Z | 4 |
| _exptl_crystal_density_diffrn [g/cm**3] | 1.326 |
| _exptl_crystal_colour | 'colorless' |
| _exptl_absorpt_coefficient_mu | 0.889 |
| _exptl_crystal_F_000 | 472 |
| _exptl_crystal_size_max/mid/min | 0.28/0.26/0.22 |

### Crystal Collection

| | |
|---|---|
| _cell_measurement_temperature | 296(2) |
| _diffrn_radiation_wavelength | 1.54178 |
| _diffrn_radiation_type | CuK\a |
| _diffrn_radiation_source | 'fine-focus sealed tube' |
| _diffrn_reflns_theta_min/max | 3.03/64.99 |
| _cell_measurement_reflns_used | 3701 |
| _cell_measurement_theta_min/max | 3.03/67.44 |

### Refinement

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_refine_ls_number_reflns                 1716
_refine_ls_number_parameters             140
_refine_ls_number_restraints             18
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_refine_ls_R_factor_gt                   0.0600
_refine_ls_wR_factor_ref                 0.1604
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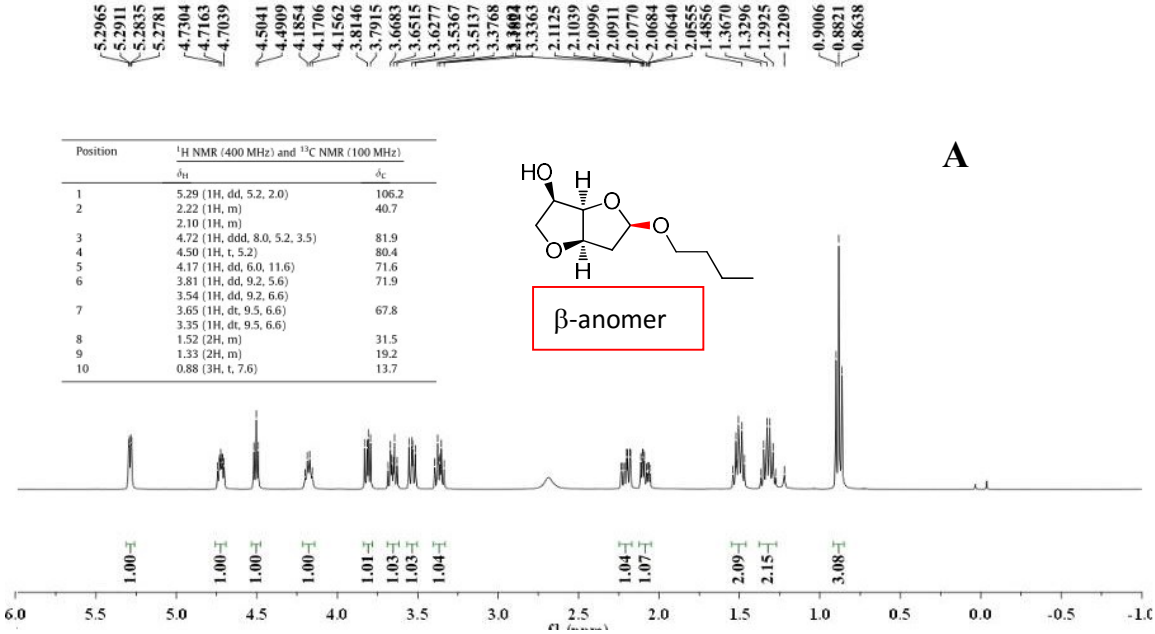
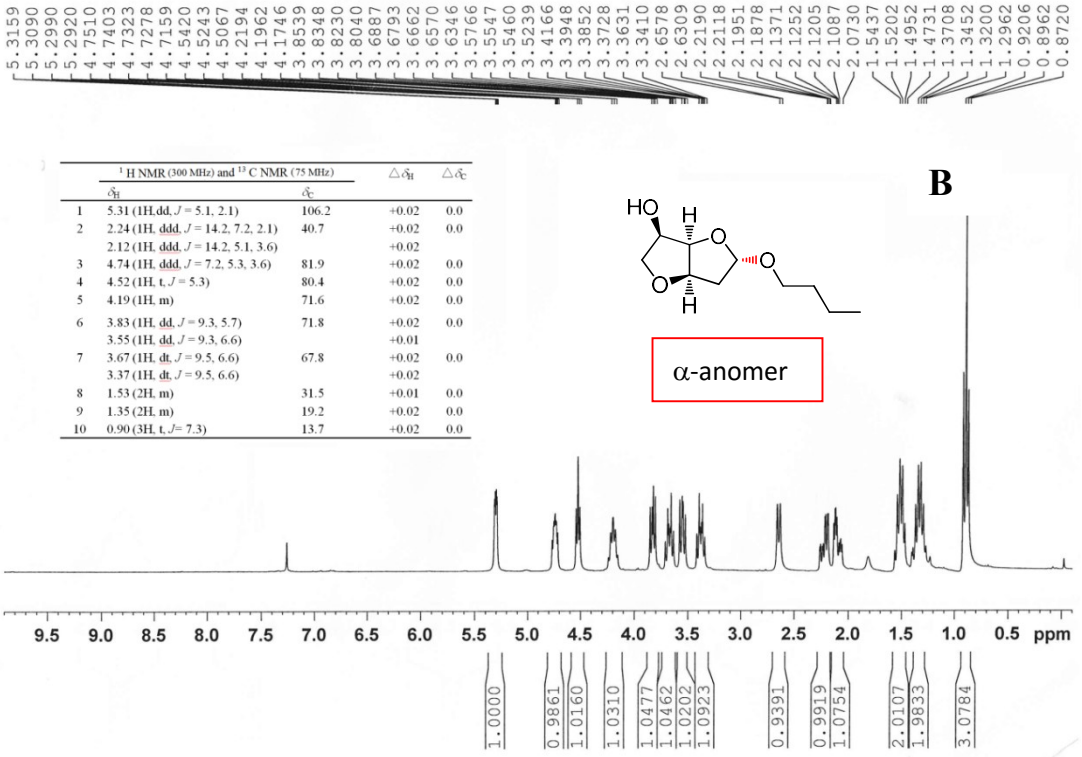
## 3. $^{1}H$ and $^{13}C$ NMR Spectra Comparation of sauropunol (A-D) obtained in this study with those previously reported.

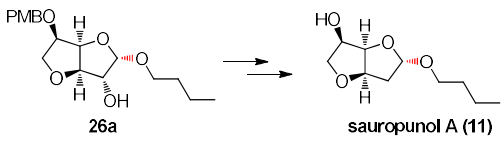
$^{1}H$ NMR spectra of sauropunol (**A**) or (**11**) isolated from *Sauropus rostratus*, **Figure A:** reported spectrum[1] and assignment; **Figure B:** our spectrum and assignment.



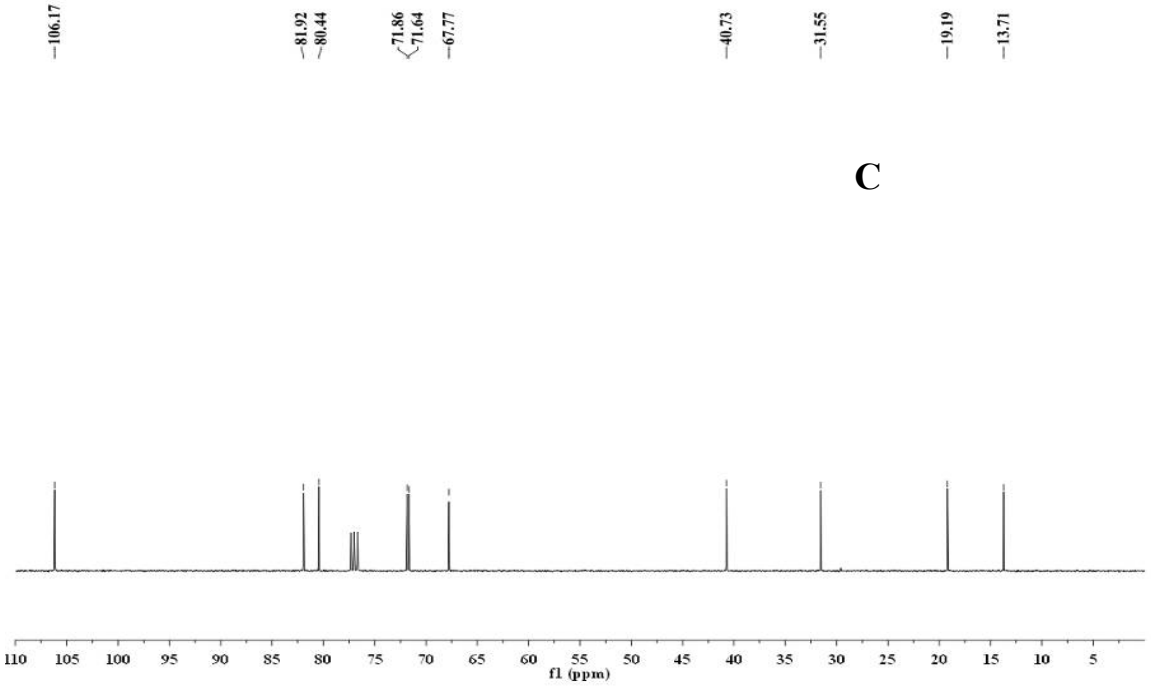

| Position | $^{1}H$ NMR (400 MHz) and $^{13}C$ NMR (100 MHz) | |
|---|---|---|
| | $\delta_H$ | $\delta_C$ |
| 1 | 5.29 (1H, dd, 5.2, 2.0) | 106.2 |
| 2 | 2.22 (1H, m) | 40.7 |
| | 2.10 (1H, m) | |
| 3 | 4.72 (1H, ddd, 8.0, 5.2, 3.5) | 81.9 |
| 4 | 4.50 (1H, t, 5.2) | 80.4 |
| 5 | 4.17 (1H, dd, 6.0, 11.6) | 71.6 |
| 6 | 3.81 (1H, dd, 9.2, 5.6) | 71.9 |
| | 3.54 (1H, dd, 9.2, 6.6) | |
| 7 | 3.65 (1H, dt, 9.5, 6.6) | 67.8 |
| | 3.35 (1H, dt, 9.5, 6.6) | |
| 8 | 1.52 (2H, m) | 31.5 |
| 9 | 1.33 (2H, m) | 19.2 |
| 10 | 0.88 (3H, t, 7.6) | 13.7 |

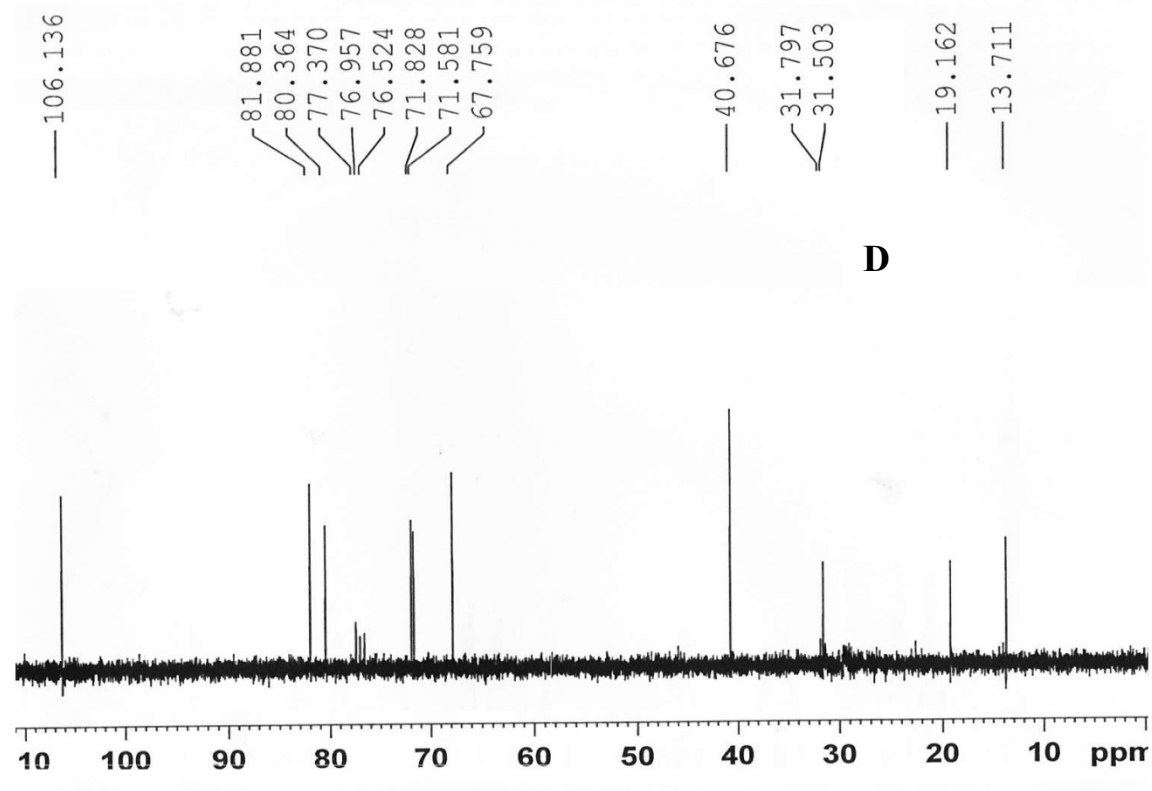



| | $^{1}H$ NMR (300 MHz) and $^{13}C$ NMR (75 MHz) | | $\Delta\delta_H$ | $\Delta\delta_C$ |
|---|---|---|---|---|
| | $\delta_H$ | $\delta_C$ | | |
| 1 | 5.31 (1H, dd, $J$ = 5.1, 2.1) | 106.2 | +0.02 | 0.0 |
| 2 | 2.24 (1H, ddd, $J$ = 14.2, 7.2, 2.1) | 40.7 | +0.02 | 0.0 |
| | 2.12 (1H, ddd, $J$ = 14.2, 5.1, 3.6) | | +0.02 | |
| 3 | 4.74 (1H, ddd, $J$ = 7.2, 5.3, 3.6) | 81.9 | +0.02 | 0.0 |
| 4 | 4.52 (1H, t, $J$ = 5.3) | 80.4 | +0.02 | 0.0 |
| 5 | 4.19 (1H, m) | 71.6 | +0.02 | 0.0 |
| 6 | 3.83 (1H, dd, $J$ = 9.3, 5.7) | 71.8 | +0.02 | 0.0 |
| | 3.55 (1H, dd, $J$ = 9.3, 6.6) | | +0.01 | |
| 7 | 3.67 (1H, dt, $J$ = 9.5, 6.6) | 67.8 | +0.02 | 0.0 |
| | 3.37 (1H, dt, $J$ = 9.5, 6.6) | | +0.02 | |
| 8 | 1.53 (2H, m) | 31.5 | +0.01 | 0.0 |
| 9 | 1.35 (2H, m) | 19.2 | +0.02 | 0.0 |
| 10 | 0.90 (3H, t, $J$= 7.3) | 13.7 | +0.02 | 0.0 |

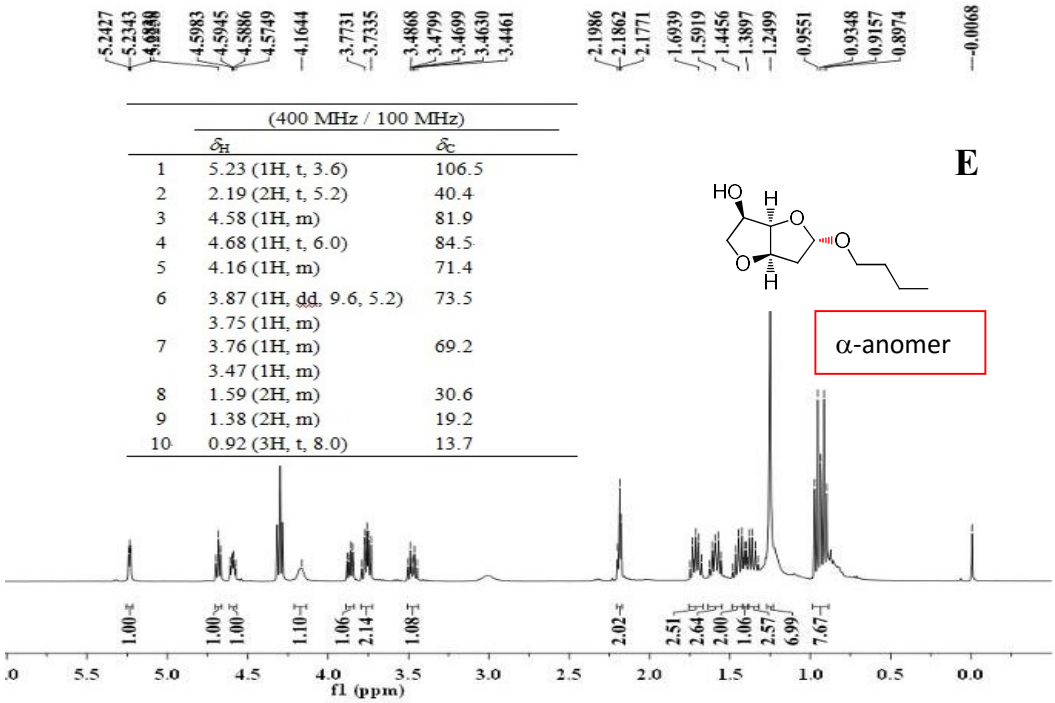


$^{13}$C NMR spectra of sauropunol (**A**) or (**11**) isolated from *Sauropus rostratus*, **Figure C:** reported spectrum[1]; **Figure D:** our spectrum.



$^{1}$H NMR spectra of **sauropunol (B)** or (**12**) isolated from *Sauropus rostratus*, **Figure E:** reported spectrum[1] and assignment; **Figure F:** our spectrum and assignment.



(400 MHz / 100 MHz)

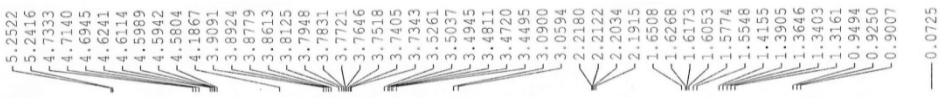
| | $\delta_H$ | $\delta_C$ |
|---|---|---|
| 1 | 5.23 (1H, t, 3.6) | 106.5 |
| 2 | 2.19 (2H, t, 5.2) | 40.4 |
| 3 | 4.58 (1H, m) | 81.9 |
| 4 | 4.68 (1H, t, 6.0) | 84.5 |
| 5 | 4.16 (1H, m) | 71.4 |
| 6 | 3.87 (1H, dd, 9.6, 5.2) | 73.5 |
| | 3.75 (1H, m) | |
| 7 | 3.76 (1H, m) | 69.2 |
| | 3.47 (1H, m) | |
| 8 | 1.59 (2H, m) | 30.6 |
| 9 | 1.38 (2H, m) | 19.2 |
| 10 | 0.92 (3H, t, 8.0) | 13.7 |

**E**



α-anomer

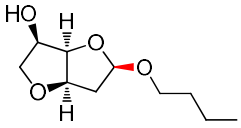




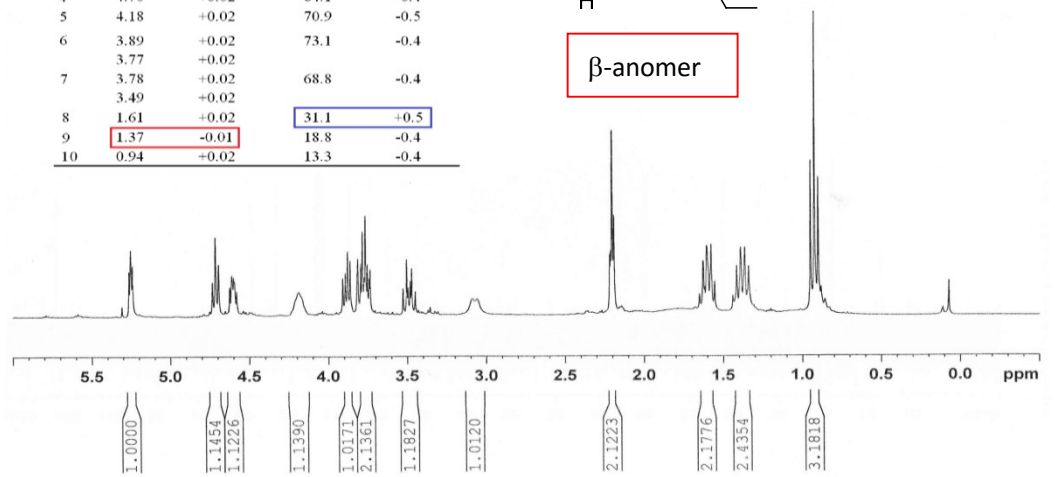
(300 MHz / 75 MHz)

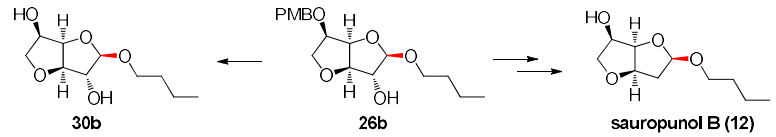
| | $\delta_H$ | $\Delta\delta_H$ | $\delta_C$ | $\Delta\delta_C$ |
|---|---|---|---|---|
| 1 | 5.25 | +0.02 | 106.1 | -0.4 |
| 2 | 2.21 | +0.02 | 39.9 | -0.5 |
| 3 | 4.60 | +0.02 | 81.4 | -0.5 |
| 4 | 4.70 | +0.02 | 84.1 | -0.4 |
| 5 | 4.18 | +0.02 | 70.9 | -0.5 |
| 6 | 3.89 | +0.02 | 73.1 | -0.4 |
| | 3.77 | +0.02 | | |
| 7 | 3.78 | +0.02 | 68.8 | -0.4 |
| | 3.49 | +0.02 | | |
| 8 | 1.61 | +0.02 | 31.1 | +0.5 |
| 9 | 1.37 | -0.01 | 18.8 | -0.4 |
| 10 | 0.94 | +0.02 | 13.3 | -0.4 |

**F**



β-anomer





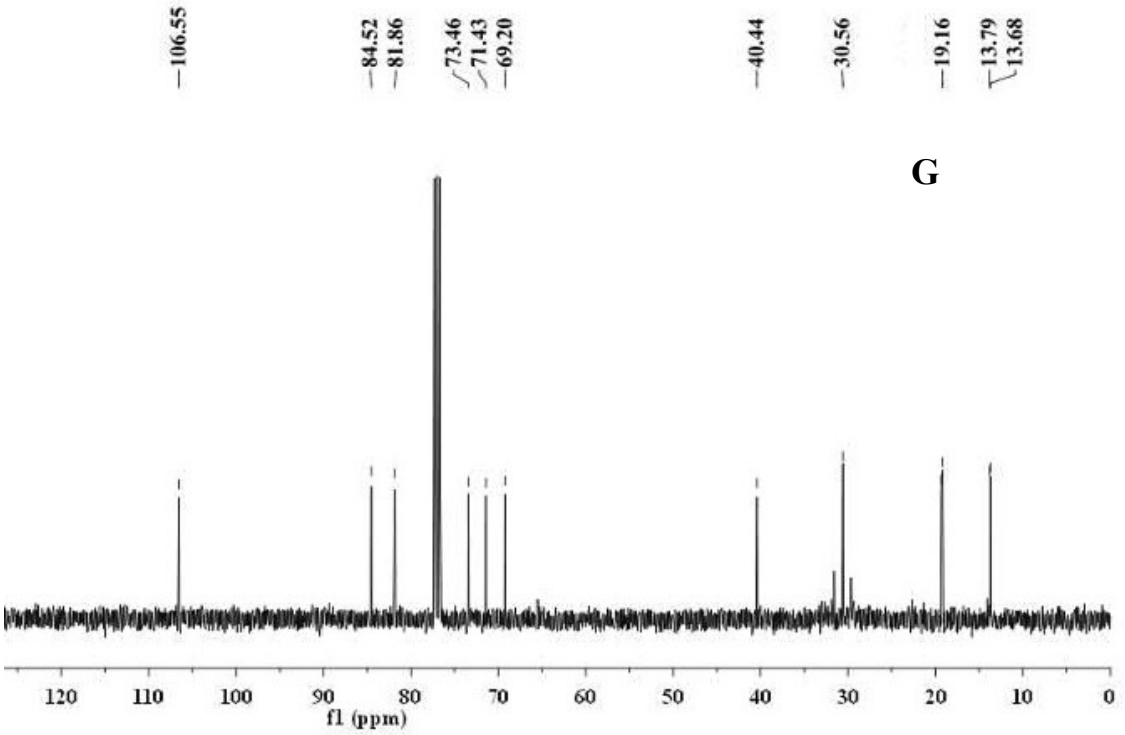
30b

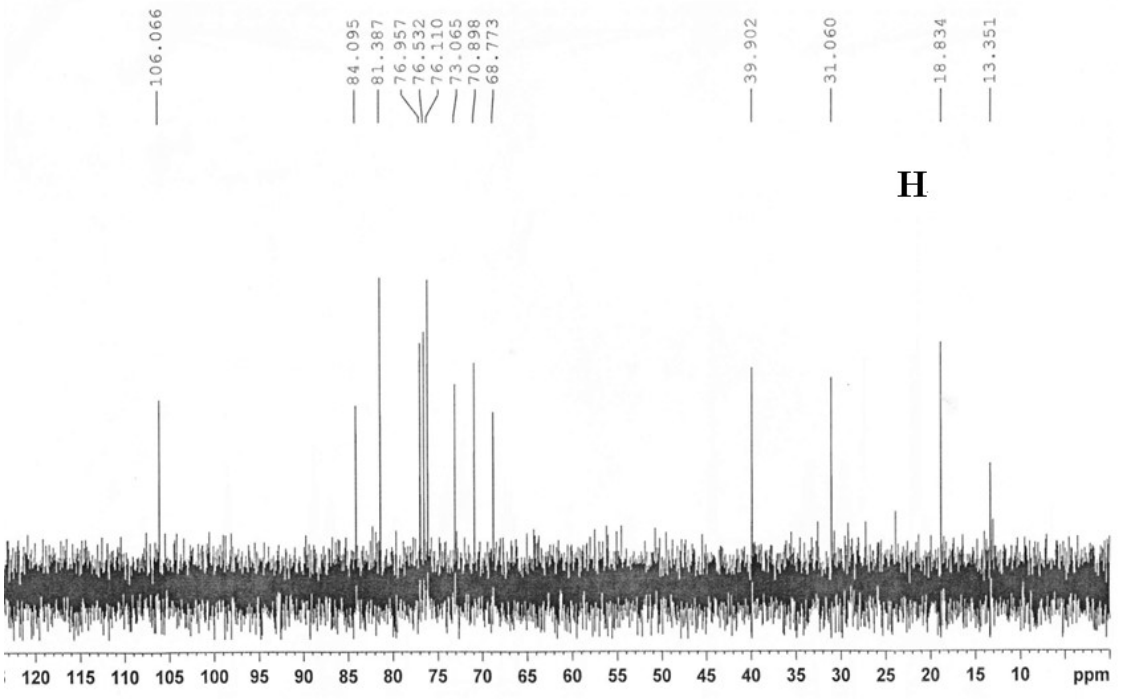
26b

sauropunol B (12)

Conformation confirmed by single crystal X-ray analysis

$^{13}$C NMR spectra of sauropunol (**B**) or (**12**) isolated from *Sauropus rostratus*, **Figure G:** reported spectrum[1]; **Figure H:** our spectrum.




Reference:
[1] Wang, C. H.; Li, W.; Liu, H. L.; Wang, J.; Li, G. Q.; Wang, G. C.; Li, Y. L. *Carbohydr. Res.* **2014**, *384*, 99-101.

## 4. Cytotoxicity assays.

The cytotoxicity of sauropunol (**A**-**D**) obtained from the present study was evaluated *via* the 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyl-tetrazolium bromide (MTT) assay on human promyelocytic leukemia cell line (HL60) and human embryonic lung fibroblast cell line (HELF) which is a kind gift from KeyGEN BioTECH. Briefly the HL60 and HELF-adherent cells were cultured in a 96-well plate overnight in $CO_2$ environment at 37°C. Supernatant was removed and 100µl serially diluted compounds with complete medium DMEM supplemented with 10% (v/v) fetal bovine serum, penicillin (100 units/ml) and streptomycin (100µg/ml) were added to each well. After the incubation, the culture medium was aspirated carefully and 50µl of MTT solution (2mg/ml PBS) was added to each well and further incubated for 4h. After this, MTT solution was aspirated and cells were PBS-washed once, and 100µl of DMSO was added to dissolve the blue insoluble MTT formazan produced by the action of mitochondrial dehydrogenase. The plate was agitated at room temperature for 15 min and then read at 570nm by using a microplate reader. The percentage of viable cells was calculated as the relative ratio of optical densities.

**Table 1.** $IC_{50}$ Values (µM) of sauropunol (**A**-**D**) against human promyelocytic leukemia cell line (HL60) and normal *HELF* cell line.

| **Compounds** | **HL60** | ***HELF*** |
|---|---|---|
| sauropunol (**A**) | >500 | >500 |
| sauropunol (**B**) | >500 | >500 |
| sauropunol (**C**/**D**) | >500 | >500 |

## 5. Anti-Inflammatory Activity Assays.

5.1. Animals

Male ICR mice were purchased from Jie Si Jie Laboratory Animals Co. (Shanghai, China). On arrival, randomized mice were transferred by 6 mice per cage and were provided with food and water *ad libitum* in a house at 22°Cunder a light-dark cycle of 12:12.Mice were used for experiment during the light phase of the cycle when their weight were between 20 to 25g.The animals were allowed to acclimate to the laboratory for over 7 days before use. Animal study and euthanasia was carried out in strict accordance with the recommendations in the Guide for the Care and Use of Laboratory Animals of the National Institutes of Health. The protocol was approved by the Committee on the Ethics of Animal Experiments of the China Pharmaceutical University.

5.2. Chemicals

TPA and indomethacin were purchased from Sigma Aldrich. Sauropunol (**A-D**) as well as intermediates **30a** and **30b** were obtained through synthesis in present study.

5.3. Mouse model of acute inflammation

Edema was induced on the right ear by topical application of 0.5 μg/ear TPA (in 20 μl acetone). To examine the effect of compounds on ear edema following topical application, groups of mice were respectively treated with 2mg/ear (in 20 μl acetone) compounds above as well as indomethacin at 30 min prior to TPA treatment. Model group received 20μl acetone at 30min prior to TPA treatment. Ear thicknesses and weights were measured 6 h after topical application of TPA.[1]

5.4. Ear edema measurement

Edema was expressed as the increase in ear thickness and ear edema rate. A punch biopsy of 6mm diameter from the Ears of mice were used for measurement 6h after TPA treatment (acetone treatment for control group). Ear thickness was measured with a digital Vernier caliper and ear weight was measured by a Electronic Balance. To minimize variation due to technique, a single investigator performed all measurements of throughout the experiment.[2] The percentage of ear edema were determined according to Delporte et al.[3] by the expression below:

$$\%\ \text{ear edema} = \frac{W_R - W_L}{W_L} \times 100$$

Where $W_R$ is the weight of the section of Right ear; $W_L$ is the weight of the section of Left ear.

5.5. Statistical analysis

All data were presented as mean±S.E.M, and statistical significance was determined *via* t-test with $p < 0.05$ considered to be significant (*$p<0.05$; **$p<0.01$).

| Group | Sex | No. | Weight/mg | | Thickness/mm | |
|---|---|---|---|---|---|---|
| | | | Left ear | Right ear | Left ear | Right ear |
| Control | Male | 1 | 9.35 | 10.41 | 0.31 | 0.37 |
| | | 2 | 7.67 | 7.15 | 0.31 | 0.31 |
| | | 3 | 8.15 | 8.58 | 0.32 | 0.35 |
| | | 4 | 9.56 | 10.23 | 0.33 | 0.41 |
| | | 5 | 8.41 | 8.24 | 0.33 | 0.27 |
| | | 6 | 10.59 | 10.42 | 0.38 | 0.38 |

| Group | Sex | No. | Weight/mg | | Thickness/mm | |
|---|---|---|---|---|---|---|
| | | | Left ear | Right ear | Left ear | Right ear |
| Model | Male | 1 | 8.17 | 20.37 | 0.32 | 0.76 |
| | | 2 | 7.87 | 23.24 | 0.3 | 0.78 |
| | | 3 | 8.06 | 25.25 | 0.32 | 0.93 |
| | | 4 | 7.98 | 22.96 | 0.32 | 0.95 |
| | | 5 | 8.09 | 22.7 | 0.35 | 0.88 |
| | | 6 | 8.07 | 21.28 | 0.2 | 0.79 |

| Group | Sex | No. | Weight/mg | | Thickness/mm | |
|---|---|---|---|---|---|---|
| | | | Left ear | Right ear | Left ear | Right ear |
| Indomet-hacin | Male | 1 | 8.01 | 9.28 | 0.28 | 0.33 |
| | | 2 | 8.05 | 10.18 | 0.29 | 0.35 |
| | | 3 | 7.48 | 9.59 | 0.3 | 0.4 |
| | | 4 | 8.77 | 13.92 | 0.32 | 0.52 |
| | | 5 | 8 | 10.58 | 0.3 | 0.43 |
| | | 6 | 8.68 | 12.96 | 0.33 | 0.57 |

| Group | Sex | No. | Weight/mg | | Thickness/mm | |
|---|---|---|---|---|---|---|
| | | | Left ear | Right ear | Left ear | Right ear |
| Sauropunol (**A**) | Male | 1 | 8.24 | 27.03 | 0.33 | 0.73 |
| | | 2 | 7.81 | 17.55 | 0.27 | 0.6 |
| | | 3 | 8.63 | 18.86 | 0.3 | 0.72 |
| | | 4 | 7.34 | 18.89 | 0.27 | 0.83 |
| | | 5 | 9.37 | 24.55 | 0.33 | 0.78 |
| | | 6 | 8.59 | 18.64 | 0.31 | 0.68 |

| Group | Sex | No. | Weight/mg | | Thickness/mm | |
|---|---|---|---|---|---|---|
| | | | Left ear | Right ear | Left ear | Right ear |
| Sauropunol (**B**) | Male | 1 | 6.7 | 12.3 | 0.28 | 0.49 |
| | | 2 | 7.8 | 12.4 | 0.34 | 0.5 |
| | | 3 | 8.9 | 13.3 | 0.3 | 0.56 |
| | | 4 | 8 | 13.8 | 0.3 | 0.55 |
| | | 5 | 8.8 | 14.6 | 0.28 | 0.56 |
| | | 6 | 8.7 | 14.2 | 0.33 | 0.48 |

| Group | Sex | No. | Weight/mg | | Thickness/mm | |
|---|---|---|---|---|---|---|
| | | | Left ear | Right ear | Left ear | Right ear |
| Sauropunol (**C/D**) | Male | 1 | 9.5 | 23.21 | 0.34 | 0.81 |
| | | 2 | 9.44 | 18.48 | 0.35 | 0.76 |
| | | 3 | 8.63 | 19.02 | 0.35 | 0.72 |
| | | 4 | 8.56 | 20.16 | 0.3 | 0.82 |
| | | 5 | 7.96 | 15.61 | 0.29 | 0.6 |
| | | 6 | 9.05 | 18.5 | 0.33 | 0.75 |

| Group | Sex | No. | Weight/mg | | Thickness/mm | |
|---|---|---|---|---|---|---|
| | | | Left ear | Right ear | Left ear | Right ear |
| **30a** | Male | 1 | 7.69 | 20.93 | 0.29 | 0.79 |
| | | 2 | 9.01 | 18.32 | 0.35 | 0.76 |
| | | 3 | 10.06 | 18.68 | 0.35 | 0.77 |
| | | 4 | 7.7 | 16.09 | 0.32 | 0.63 |
| | | 5 | 8.57 | 16.36 | 0.35 | 0.73 |
| | | 6 | 8.79 | 16.1 | 0.27 | 0.64 |

| Group | Sex | No. | Weight/mg | | Thickness/mm | |
|---|---|---|---|---|---|---|
| | | | Left ear | Right ear | Left ear | Right ear |
| **30b** | Male | 1 | 7.29 | 10.06 | 0.27 | 0.29 |
| | | 2 | 8.68 | 18.57 | 0.29 | 0.52 |
| | | 3 | 7.43 | 17.85 | 0.25 | 0.72 |
| | | 4 | 9.22 | 19.93 | 0.3 | 0.76 |
| | | 5 | 7.6 | 16.29 | 0.27 | 0.59 |
| | | 6 | 8.04 | 18.55 | 0.33 | 0.65 |

Reference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