Diverse Motifs of Mannoside-Clustering on a β -Cyclodextrin Core

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Supporting Information (31 Pages)

Data for 2: ^1H NMR (300 MHz, CDCl_3): δ 5.15 (d, 7H, $^3J_{1,2}$ = 3.3 Hz, H-1), 4.29 (dd, 7H, 2J = 16.0 Hz, 4J = 2.5 Hz, $\text{OCHC}\equiv$), 4.22 (dd, 7H, 2J = 15.8 Hz, 4J = 2.4 Hz, $\text{OCH}'\text{C}\equiv$), 4.15 (dd, 7H, $^3J_{2,3}$ = 7.3 Hz, $^3J_{3,4}$ = 5.5 Hz, H-3), 4.10 (bs, 7H, H-6), 3.84 (dd, 7H, $^3J_{4,5}$ = 7.6 Hz, $^3J_{3,4}$ = 5.5 Hz, H-4), 3.78 (m, 7H, H-5), 3.72 (dd, 7H, $^2J_{6,6'}$ = 10.9 Hz, $^3J_{5,6'}$ = 1.8 Hz, H-6'), 3.50 (dd, 7H, $^3J_{2,3}$ = 7.3 Hz, $^3J_{1,2}$ = 2.9 Hz, H-2), 2.40 (t, 7H, 4J = 2.2 Hz, $\equiv\text{CH}$), 0.90 (s, 63H, $\text{OSiC}(\text{CH}_3)_3$), 0.89 (s, 63H, $\text{OSiC}(\text{CH}_3)_3$), 0.13 (s, 21H, OSiCH_3), 0.12 (s, 21H, OSiCH_3), 0.04 (s, 42H, OSiCH_3). ^{13}C NMR (75.5 MHz, CDCl_3): δ 97.0 (C-1), 79.9 ($-\text{C}\equiv$), 77.8 (C-4), 77.2 (C-2), 74.8 ($\equiv\text{CH}$), 73.2 (C-5), 72.7 (C-3), 62.5 (C-6), 57.3 ($\text{OCH}_2\text{C}\equiv$), 26.4, 26.1 ($\text{OSiC}(\text{CH}_3)_3$), 18.3, 18.2 ($\text{OSiC}(\text{CH}_3)_3$), -3.6, -3.7, -4.7, -5.0 (OSiCH_3). MALDI-TOF: m/z 3023.23 $[\text{M}+\text{Na}]^+$.

Data for 4: ^1H NMR (300 MHz, CDCl_3): δ 7.50-7.22 (m, 70H, Ph), 5.12 (d, 7H, $^3J_{1,2}$ = 3.3 Hz, H-1), 4.84 (d, 7H, 2J = 12.0 Hz, C2- OCHPh), 4.79 (d, 7H, 2J = 12.0 Hz, C2- $\text{OCH}'\text{Ph}$), 4.56 (dd, 7H, 2J = 15.3 Hz, 4J = 2.7 Hz, $\text{OCHC}\equiv$), 4.50 (dd, 7H, 2J = 15.6 Hz, 4J = 2.4 Hz, $\text{OCH}'\text{C}\equiv$), 4.37 (s, 14H, C6- OCH_2Ph), 3.95-3.83 (m, 28H, H-3,4,5,6), 3.49 (bd, 7H, $^2J_{6,6'}$ = 10.8 Hz, H-6'), 3.45 (dd, 7H, $^3J_{2,3}$ = 9.8 Hz, $^3J_{1,2}$ = 3.5 Hz, H-2), 2.43 (t, 7H, 4J = 2.3 Hz, $\equiv\text{CH}$). ^{13}C NMR (75.5 MHz, CDCl_3): δ 138.4, 138.1, 128.2, 128.0, 127.6, 127.5, 127.4 (Ph), 98.9 (C-1), 81.2 ($-\text{C}\equiv$), 79.6, 79.3 (C-3,4,5), 78.8 (C-2), 74.0 ($\equiv\text{CH}$), 73.1, 73.0 (OCH_2Ph), 71.2 (C-3,4,5), 68.9 (C-6), 60.6 ($\text{OCH}_2\text{C}\equiv$). MALDI-TOF: m/z 2686.00 $[\text{M}+\text{Na}]^+$.

Data for 5: ^1H NMR (300 MHz, CDCl_3): δ 4.97 (d, 7H, $^3J_{1,2}$ = 3.9 Hz, H-1), 4.75 (s, 7H, OH), 4.45 (dd, 14H, 4J = 2.4 Hz, C2- $\text{OCH}_2\text{C}\equiv$), 4.30 (dd, 7H, 2J = 15.8 Hz, 4J = 2.5 Hz, C6- $\text{OCHC}\equiv$), 4.19 (dd, 7H, 2J = 16.0 Hz, 4J = 2.4 Hz, C6- $\text{OCH}'\text{C}\equiv$), 3.94 (t, 7H, 3J = 9.5 Hz, H-3), 3.93 (d, 7H, H-6), 3.80-3.73 (m, 7H, H-5), 3.77 (dd, 7H, $^2J_{6,6'}$ = 10.2 Hz, $^3J_{5,6'}$ = 1.4 Hz, H-6'), 3.69 (dd, 7H, $^3J_{2,3}$ = 9.7 Hz, $^3J_{1,2}$ = 3.8 Hz, H-2), 3.48 (t, 7H, 3J = 9.3 Hz, H-4), 2.50 (t, 7H, 4J = 2.3 Hz, C6- $\text{OCH}_2\text{C}\equiv\text{CH}$), 2.46 (t, 7H, 4J = 2.4 Hz, C2- $\text{OCH}_2\text{C}\equiv\text{CH}$). ^{13}C NMR (75.5 MHz, CDCl_3): δ 101.7 (C-1), 83.3 (C-4), 79.6 (C6- $\text{OCH}_2\text{C}\equiv$), 79.2 (C2- $\text{OCH}_2\text{C}\equiv$), 78.3 (C-2), 75.4 (C2- $\text{OCH}_2\text{C}\equiv\text{CH}$), 74.9 (C6- $\text{OCH}_2\text{C}\equiv\text{CH}$), 73.4 (C-3), 70.0 (C-5), 68.2 (C-6), 59.4 (C2- $\text{OCH}_2\text{C}\equiv$), 58.4 (C6- $\text{OCH}_2\text{C}\equiv$). MALDI-TOF: m/z 1690.57 $[\text{M}+\text{Na}]^+$.

Data for 6: ^1H NMR (300 MHz, CDCl_3): δ 5.19 (d, 7H, $^3J_{1,2}$ = 3.6 Hz, H-1), 4.62 (dd, 7H, 2J = 15.4 Hz, 4J = 2.4 Hz, C3- $\text{OCHC}\equiv$), 4.47 (dd, 7H, 2J = 16.4 Hz, 4J = 2.4 Hz, C3- $\text{OCH}'\text{C}\equiv$), 4.44 (t, 14H, 4J = 2.4 Hz, C2- $\text{OCH}_2\text{C}\equiv$), 4.27 (dd, 7H, 2J = 15.9 Hz, 4J = 2.3 Hz, C6- $\text{OCHC}\equiv$), 4.18 (dd, 7H, 2J = 15.9 Hz, 4J = 2.3 Hz, C6- $\text{OCH}'\text{C}\equiv$), 3.93-3.79 (m, 21H, H-5,6,6'), 3.82 (t, 7H, 3J = 9.7 Hz, H-3), 3.71 (t, 7H, 3J = 9.4 Hz, H-4), 3.59 (dd, 7H, $^3J_{2,3}$ = 9.7 Hz, $^3J_{1,2}$ = 3.6 Hz, H-2), 2.50 (t, 7H, 4J = 2.4 Hz, C3,6- $\text{OCH}_2\text{C}\equiv\text{CH}$), 2.48 (t, 7H, 4J = 2.4 Hz, C3,6- $\text{OCH}_2\text{C}\equiv\text{CH}$), 2.44 (t, 7H, 4J = 2.4 Hz, C2- $\text{OCH}_2\text{C}\equiv\text{CH}$). ^{13}C NMR (75.5 MHz, CDCl_3): δ 99.3 (C-1), 80.9 (C3- $\text{OCH}_2\text{C}\equiv$), 80.0 (C2,6- $\text{OCH}_2\text{C}\equiv$), 79.8, 79.6 (C-4,5), 79.6 (C2,6- $\text{OCH}_2\text{C}\equiv$), 78.0 (C-2), 74.9, 74.8 (C2,6- $\text{OCH}_2\text{C}\equiv\text{CH}$), 74.0 (C3- $\text{OCH}_2\text{C}\equiv\text{CH}$), 70.6 (C-3), 68.6 (C-6), 60.7 (C3- $\text{OCH}_2\text{C}\equiv$), 58.7 (C2- $\text{OCH}_2\text{C}\equiv$), 58.4 (C6- $\text{OCH}_2\text{C}\equiv$). MALDI-TOF: m/z 1956.49 $[\text{M}+\text{Na}]^+$.

Data of 8: ^1H NMR (300 MHz, CDCl_3): δ 7.33 (d, 14H, 3J = 8.6 Hz, Ph), 7.00 (d, 14H, 3J = 8.6 Hz, Ph), 5.53 (dd, 7H, $^3J_{3',4'}$ = 10.0 Hz, $^3J_{2',3'}$ = 3.6 Hz, H-3'), 5.51 (s, 7H, H-1'), 5.43 (bs, 7H, H-2'), 5.34 (t, 7H, 3J = 10.2 Hz, H-4'), 5.23 (bs, 7H, H-1), 4.58 (d, 7H, 2J = 16.8 Hz, OCH_2), 4.46 (d, 7H, 2J = 16.8 Hz, OCH_2), 4.29 (m, 7H, H-6'), 4.28-4.03 (m, 21H, H-3,5,6), 4.09-4.02 (m, 14H, H-5',6'), 3.84 (bs, 7H, H-4), 3.75 (bs, 7H, H-6), 3.72 (bs, 7H, H-2), 2.19-2.00 (4s, 84H, 28 CH_3CO), 0.87, 0.85 (2s, 126H, 2 $\text{OSiC}(\text{CH}_3)_3$),

0.15-0.02 (3s, 84H, 4 OSiCH₃). ¹³C NMR (75.5 MHz, CDCl₃): δ 170.4-169.7 (CO), 155.3, 133.2, 117.6, 116.2 (Ph), 97.1 (C-1), 95.6 (C-1'), 86.0, 84.7 (C≡C), 78.2 (C-4), 77.2 (C-2), 72.7 (C-3,5), 69.2, 68.7 (C-2',3',5'), 65.8 (C-4'), 62.7 (C-6), 62.0 (C-6'), 57.1 (OCH₂), 26.3, 26.0 (SiC(CH₃)₃), 20.8-20.6 (CH₃CO), 18.2 (SiC(CH₃)₃), -3.6, -4.7, -5.0 (SiCH₃). MALDI-TOF: m/z 5981.06 [M+Na]⁺.

Data for 9: ¹H NMR (300 MHz, CDCl₃): δ 7.54 (d, 14H, ³J = 6.8 Hz, Ph), 7.28-7.20 (m, 70H, Bn), 6.97 (d, 14H, ³J = 8.8 Hz, Ph), 5.53 (dd, 7H, ³J_{3',4'} = 10.5 Hz, ³J_{2',3'} = 3.7 Hz, H-3'), 5.50 (s, 7H, H-1'), 5.43 (bs, 7H, H-2'), 5.35 (t, 7H, ³J = 10.0 Hz, H-4'), 5.08 (d, 7H, ³J_{1,2} = 2.4 Hz, H-1), 4.91 (m, 21H, OCH₂Ph, OCH₂C≡), 4.69 (d, 7H, ²J = 13.8 Hz, OCH₂C≡), 4.33 (s, 14H, OCH₂Ph), 4.27 (m, 7H, H-6'), 4.05 (m, 14H, H-5',6'), 3.79 (m, 28H, H-3,4,5,6), 3.47 (m, 14H, H-2,6), 2.20-1.97 (4s, 84H, 28 CH₃CO). ¹³C NMR (75.5 MHz, CDCl₃): δ 170.4-169.7 (CO), 155.3 (Ph), 138.4, 138.0 (Bn), 133.2 (Ph), 128.2, 127.5 (Bn), 117.5, 116.3 (Ph), 99.3 (C-1), 95.6 (C-1'), 86.0, 84.6 (C≡C), 81.1, 79.7 (C-4,5), 78.4 (C-2), 73.2, 73.0 (OCH₂Ph), 71.2 (C-3), 69.2, 68.8 (C-2',3',5'), 69.0 (C-6), 65.9 (C-4'), 62.0 (C-6'), 61.8 (OCH₂C≡), 20.8-20.5 (CH₃CO). MALDI-TOF: m/z 5648.30 [M+Na]⁺.

Data for 10: ¹H NMR (300 MHz, DMSO-d₆, 80° C): δ 7.56-7.44 (m, 28H, Ph), 7.22-7.17 (m, 28H, Ph), 5.78, 5.71 (bs, 14H, H-1'), 5.44 (m, 28H, H-2',3'), 5.27 (t, 14H, ³J = 9.6 Hz, H-4'), 4.64 (bs, 14H, OCH₂), 4.42 (bs, 14H, OCH₂), 4.23-4.05 (m, 42H, H-5',6',6'), 2.23-1.97 (8s, 168H, 56 CH₃CO). ¹³C NMR (75.5 MHz, DMSO-d₆, 80° C): δ 169.3-169.0 (CO), 154.9, 132.5, 116.9, 116.4 (Ph), 98.0 (C-1), 95.2 (C-1'), 85.6, 85.0 (C≡C), 68.8, 68.3, 68.2 (C-2',3',5'), 65.5 (C-4'), 61.5 (C-6'), 58.3 (OCH₂C≡), 19.9-19.8 (CH₃CO). MALDI-TOF: m/z 7728.57 [M+Na-4Ac]; 7898.61 [M+Na]⁺.

Data for 11: ¹H NMR (300 MHz, DMSO-d₆, 80° C): δ 7.47-7.43 (m, 42H, Ph), 7.16-7.10 (m, 42H, Ph), 5.72, 5.70 (bs, 21H, H-1'), 5.45 (m, 42H, H-2',3'), 5.37 (bs, 7H, H-1), 5.26 (t, 21H, ³J = 9.6 Hz, H-4'), 5.00 (bd, 7H, ²J = 14.4 Hz, OCH₂), 4.80 (bs, 14H, OCH₂), 4.74 (bd, 7H, ²J = 14.4 Hz, OCH₂), 4.46 (d, 7H, OCH₂), 4.40 (d, 7H, OCH₂), 4.20 (dd, 21H, ²J = 11.7 Hz, ³J = 5.2 Hz, H-6'), 4.23-4.04 (m, 42H, H-5',6'), 3.72 (bd, 7H, ³J = 6.6 Hz, H-2), 2.23-1.93 (10s, 252H, 84 CH₃CO). ¹³C NMR (75.5 MHz, DMSO-d₆, 80° C): δ 169.1-168.8 (CO), 154.7, 132.3, 116.7, 116.1 (Ph), 98.4 (C-1), 95.1 (C-1'), 86.0-83.8 (C≡C), 79.9, 79.4 (C-4,5), 77.5 (C-2), 70.6 (C-3), 68.6, 68.2, 68.1 (C-2',3',5'), 65.3 (C-4'), 61.4 (C-6'), 60.6 (C-6), 58.3 (OCH₂C≡), 19.8-19.6 (CH₃CO). MALDI-TOF: m/z 10824.36 [M+Na]⁺.

Data for 12: ¹³C NMR (75.5 MHz, DMSO-d₆, 80° C): δ 156.6, 132.9, 116.8, 115.0 (Ph), 100.2 (C-1), 98.6 (C-1'), 86.2, 84.3 (C≡C), 82.0 (C-4), 78.7 (C-2), 75.0, 70.5, 69.9 (C-2',3',5'), 72.9 (C-5), 71.5 (C-3), 66.6 (C-4'), 60.9 (C-6'), 59.4 (C-6), 57.5 (OCH₂C≡). MALDI-TOF: m/z 3204.20 [M+Na]⁺.

Data for 13: ¹³C NMR (75.5 MHz, DMSO-d₆, 80° C): δ 154.3, 135.2, 128.5, 116.5 (Ph), 100.7 (C-1), 99.1 (C-1'), 81.4, 77.8, 72.6, 72.1 (C-2,3,4,5), 70.9 (C-6), 74.1, 70.5, 69.8 (C-2',3',5'), 66.8 (C-4'), 60.9 (C-6'), 59.8 (OCH₂), 31.3, 30.6 (CH₂). MALDI-TOF: m/z 3232.20 [M+Na]⁺.

Data for 14: ¹³C NMR (75.5 MHz, DMSO-d₆, 80° C): δ 156.2, 132.4, 116.6, 115.2 (Ph), 100.2 (C-1), 98.7 (C-1'), 85.9-83.9 (C≡C), 74.4, 70.4, 69.5 (C-2',3',5'), 67.0 (C-4'), 60.8 (C-6'), 59.2, 58.3 (OCH₂C≡).

Data for 15: ^{13}C NMR (75.5 MHz, DMSO- d_6 , 80° C): δ 156.5, 132.9, 116.7, 115.2 (Ph), 99.0 (C-1), 98.6 (C-1'), 86.0-84.3 ($\text{C}\equiv\text{C}$), 80.3, 80.2, 77.4, 77.3 (C-2,3,4,5), 74.9, 70.5, 69.9 (C-2',3',5'), 66.5 (C-4'), 60.8 (C-6'), 59.2, 58.5 ($\text{OCH}_2\text{C}\equiv$). MALDI-TOF: m/z 7300.50 $[\text{M}+\text{Na}]^+$.

Compound 2

Compound 2

Compound 4

Compound **4**

Compound 5

Compound **5**

Compound 6

Compound 6

Compound 8

Compound **8**

Compound 9

Compound **9**

Compound 10

Compound **10**

Compound 11

Compound 11

Compound 12

Compound 13

Compound 14

Compound 15

Compound 8

Compound 9

Applied Biosystems voyager system zvo i

Voyager Spec #1=>NF0.1(BP = 5648.2, 4736)

Mode of operation: Linear
Extraction mode: Delayed
Polarity: Positive
Acquisition control: Manual
Accelerating voltage: 25000 V
Grid voltage: 91.5%
Guide wire 0: 0.06%
Extraction delay time: 320 nsec
Acquisition mass range: 1000 – 10000 Da
Number of laser shots: 200/spectrum
Laser intensity: 2766
Laser Rep Rate: 3.0 Hz
Calibration type: External -- D:\data\masses\Antonia\A. Vargas\calmix3_7oct2002.ca
Calibration matrix: Sinapinic acid
Low mass gate: 900 Da
Digitizer start time: 19.936
Bin size: 2 nsec
Number of data points: 21296
Vertical scale: 200 mV
Vertical offset: 0%
Input bandwidth: 500 MHz

Sample well: 44
Plate ID: INSTALL
Serial number: 2081
Instrument name: Voyager-DE RP
Plate type filename: C:\VOYAGER\100 well plate.pit
Lab name: Servei Espectrometria de Masses

Absolute x-position: 15989.2
Absolute y-position: 26110.9
Relative x-position: -838.297
Relative y-position: -876.636
Shots in spectrum: 400
Source pressure: 1.485e-007
Mirror pressure: 6.018e-008
TC2 pressure: 0.001
TIS gate width: 21
TIS flight length: 942.5

Acquired: 09:56:00, October 07, 2002
Bn26M3CD / DHB
D:\data\masses\Antonia\A. Vargas\7oct2002_0010.dat

Printed: 09:57, October 07, 2002

Compound 10

Man26CD / DHB (CHCl3:CH3CN 2:1)
D:\...Avargas8mag02_0009.dat

Compound 11

Applied Biosystems voyager system 4001

Voyager Spec #1=NR(0.30)[BP = 10824.8, 3953]

Site ① > 4000 u/e

Mode of operation: Linear
Extraction mode: Delayed
Polarity: Positive
Acquisition control: Manual

Accelerating voltage: 25000 V
Gnd voltage: 91.5%
Guide wire 0: 0.05%
Extraction delay time: 300 nsec

Acquisition mass range: 2000 -- 15000 Da
Number of laser shots: 100/spectrum
Laser intensity: 2452
Laser Rep Rate: 3.0 Hz
External -- D:\data\masses\Irene\Sucres\AVargas8maig02_calmix3dht
Calibration type: 2.5-Dihydroxybenzoic acid
Calibration matrix: 1000 Da
Low mass gate:

Digitizer start time: 23.086
Bin size: 2 nsec
Number of data points: 24209
Vertical scale: 200 mV
Vertical offset: 0%
Input bandwidth: 500 MHz

Sample well: 37
Plate ID: INSTALL
Serial number: 2081
Instrument name: Voyager-DE RP
Plate type filename: C:\VOYAGER\100 well plate.plt
Lab name: Servei Espectrometria de Masses

Absolute x-position: 31933.9
Absolute y-position: 31255.9
Relative x-position: -133.615
Relative y-position: -811.584
Shots in spectrum: 83
Source pressure: 2.071e-007
Mirror pressure: 6.126e-008
TC2 pressure: 0.001
TIS gate width: 21
TIS flight length: 942.5

Compound 12

Applied Biosystems Voyager System 2081

Voyager Spec #1 [BP = 609.5, 3187]

Mode of operation: Reflecton
Extraction mode: Delayed
Polarity: Positive
Acquisition control: Manual

Accelerating voltage: 20000 V
Grid voltage: 66%
Mirror voltage ratio: 1.06
Guide wire 0: 0.06%
Extraction delay time: 320 nsec

Acquisition mass range: 500 - 5000 Da
Number of laser shots: 200/spectrum
Laser intensity: 2840
Laser Rep Rate: 3.0 Hz
Calibration type: External - D:\data\masses\AntoniaA. Vargas\07oct2002\calmix2.c
Calibration matrix: a-Cyano-4-hydroxycinnamic acid
Low mass gate: 400 Da
Timed ion selector: Off

Digitizer start time: 23.054
Bin size: 2 nsec
Number of data points: 24788
Vertical scale 0: 1000 mV
Vertical offset: 1%
Input bandwidth 0: 500 MHz

Sample well: 36
Plate ID: INSTALL
Serial number: 2081
Instrument name: Voyager-DE RP
Plate type filename: C:\VOYAGER\100 well plate.plt
Lab name: Servei Espectrometria de Masses

Absolute x-position: 26946.4
Absolute y-position: 31418.3
Relative x-position: -41.0564
Relative y-position: -649.214
Shots in spectrum: 400
Source pressure: 1.627e-007
Mirror pressure: 6.234e-008
TC2 pressure: 0.001
TIS gate width: 21
TIS flight length: 942.5

Acquired: 09:21:00, October 07, 2002
Man2CD2 / DHB
D:\data\masses\AntoniaA. Vargas\07oct2002_0005.dat

Printed: 09:25, October 07, 2002

Compound 13

new biosystems voyager system 4202

Voyager Spec #1=>NR(0.15)[BP = 2834.9, 1659]

Mode of operation: Reflector
Extraction mode: Delayed
Polarity: Positive
Acquisition control: Manual

Accelerating voltage: 20000 V
Grid voltage: 65%
Mirror voltage ratio: 1.12
Guide wire 0: 0%
Extraction delay time: 300 nsec

Acquisition mass range: 1200 – 6000 Da
Number of laser shots: 500/spectrum
Laser intensity: 2563
Laser Rep Rate: 20.0 Hz
Calibration type: External – D:\Data\irenelvarisAVargas6nov02_calmix2.cal
Calibration matrix: a-Cyano-4-hydroxycinnamic acid
Low mass gate: 850 Da
Timed ion selector: Off

Digitizer start time: 50.7715
Bin size: 0.5 nsec
Number of data points: 125226
Vertical scale 0: 500 mV
Vertical offset: 1%
Input bandwidth 0: 500 MHz

Sample well: 79
Plate ID: PLATE 1
Serial number: 4262
Instrument name: Voyager-DE STR
Plate type filename: C:\Voyager\100 well plate.plt
Lab name: PE Biosystems

Absolute x-position: 42488.3
Absolute y-position: 10895.4
Relative x-position: 260.847
Relative y-position: -852.136
Shots in spectrum: 2000
Source pressure: 1.454e-007
Mirror pressure: 1.337e-008
TC2 pressure: 0.01464
TIS gate width: 8
TIS flight length: 1183

d: 10:06:00, November 06, 2002
Zh / DHB
irenelvarisAVargas6nov02_0003.dat

Printed: 10:09, November 06, 2002

Compound 15