Monosaccharides: A ToF-SIMS reference spectra database. II. Positive polarity

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The number of time-of-flight secondary ion mass spectrometry studies on biological tissues and cells has strongly increased since the development of primary ion sources that allow not only elemental but also molecular analysis. Substantial fragmentation during ionic bombardment results in a large number of peaks, rendering data analysis complex. Complete and trustable sets of reference spectra for the main biological building blocks, i.e., amino acids, monosaccharides, fatty acids, and nucleotides, are required. This work aims to provide an accurate and extensive library of reference spectra for monosaccharides, measured with the Bi_3^+ primary ion. Here (Paper II), the positive polarity spectra and lists of associated characteristic fragments are presented. *Published by the AVS.*

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Keywords: ToF-SIMS, carbohydrate, sugar, monosaccharide, mass spectrometry, fragmentation

INTRODUCTION

Monosaccharides are the building blocks of structural polymers of both plant [e.g., cellulose, pectins, and hemicelluloses (Refs. 1 and 2)] and animal origin [e.g., chitin (Refs. 3 and 4)] and are essential components of glycoproteins (Refs. 5–7). Monosaccharides, their derivatives, and polymers are also indispensable in cellular respiration (Ref. 8) and for energy storage and transport in biological organisms (Refs. 9 and 10). Further, specific monosaccharides and monosaccharide derivatives act as secondary messengers [e.g., inositol 1,4,5-triphosphate in Ca^{2+} release (Ref. 11)], as essential reagents in detoxification [e.g., glucuronic acid in phase II liver metabolism (Ref. 12)], and as markers mediating cell-cell interaction (Ref. 13).

A time-of-flight secondary ion mass spectrometry (ToF-SIMS) study of seven selected hexoses was presented by Berman *et al.* based on the analysis of positive secondary ions produced by the bombardment with Au^+ primary ions (Ref. 14). They could demonstrate the fragmentation pathway of glucose via the loss of successive water molecules. Interestingly, they also found that different isomers undergo different fragmentation patterns, which shows that ToF-SIMS is a powerful tool to obtain an accurate differentiation of monosaccharides. The work presented here provides a library of ToF-SIMS reference spectra for the monosaccharides allose, arabinose, fructose, fucose, galactose, 2-deoxy-galactose, galacturonic acid, glucose, glucuronic acid, mannose, myo-inositol, rhamnose, ribose, 2-deoxy-ribose, xylose, *N*-acetylgalactosamine, *N*-acetylglucosamine, *N*-acetylmuramic acid, and *N*-acetylneuraminic acid. Characteristic fragments are listed beside the spectra for each monosaccharide. This part (Paper II) of the monosaccharide database contains the positive polarity spectra. The negative spectra are published in Paper I (Ref. 15). Analog databases for the full set of proteinogenic amino acids + glycine (Refs. 16 and 17) are available. Peak lists (Ref. 18) and reference spectra (Ref. 19) for selected lipids can be found in the literature.

The monosaccharides were purchased in the form of pure powders. D-Galacturonic acid and D-glucuronic acid were from

Fluka and all others from Sigma Aldrich. Each powder was dissolved in freshly de-ionized H_2O (resistivity $>18.2 \text{ M}\Omega \text{ cm}$) at a concentration of 0.1M. Host silicon wafers of $1 \times 1 \text{ cm}^2$ size were first washed by submersion in subsequent ultrasound baths of $2 \times 15 \text{ min}$ in acetone and $1 \times 15 \text{ min}$ in ethanol and then plasma-treated for a duration of 10 min to render the surface hydrophilic. 50 μl of solution was then deposited on the pretreated silicon wafer substrates, and the water was allowed to evaporate in a fume hood at room temperature.

The spectra were acquired on a ToF-SIMS 5 instrument (IONTOF GmbH) with a 25 keV Bi_3^+ primary ion beam operated in high mass resolution spectral mode. The primary ion dose density was kept below the static limit ($\leq 10^{12} \text{ ions/cm}^2$). Four to ten randomly selected areas of $200 \times 200 \mu\text{m}^2$ ($128 \times 128 \text{ pixels}^2$, 50 scans) were analyzed for each monosaccharide sample, to insure good reproducibility. No electron flood gun was used. All spectra were normalized to their respective total ions count. The most relevant characteristic fragments are displayed directly on the spectra and reported in the tables. Intact monosaccharide molecules are referred to as “*M*,” contaminants as “*c*,” and cationization products as “*c.p*.” Major peaks where a unique attribution was not possible, e.g., due to overlap beyond the mass resolution of two potential fragmentation products, are marked with “*n.a.*” standing for *not (uniquely) attributed*. The deviation values for all assigned peaks are below 150 ppm. The peak assignments to the fragmentation species given in the tables are tentative, and the smaller fragments are nonspecific. The unfragmented molecular ion $[\text{M}+\text{H}]^+$ displays a low signal-to-noise ratio for all monosaccharides except amino sugars and myo-inositol. All monosaccharides show strong $[\text{M}-n(\text{H}_2\text{O})+\text{H}]^+$ peaks.

Raw data (ASCII) are included in the supplementary material (Ref. 20).

SPECIMEN DESCRIPTION

Accession #: 01592, 01593, 01594, 01595, 01596, 01597, 01598, 01599, 01600, 01601, 01602, 01603, 01604, 01605, 01606, 01607, 01608, 01609, 01610

Host Material: Silicon (100) wafer

CAS Registry #: D-Allose: 2595-97-3, L-arabinose: 87-72-9, D-fructose: 57-48-7, D-fucose: 3615-37-0, D-galactose: 59-23-4,

Accession #: 01592, 01593, 01594, 01595, 01596, 01597, 01598, 01599, 01600, 01601, 01602, 01603, 01604, 01605, 01606, 01607, 01608, 01609, 01610

Technique: SIMS

Host Material: Silicon (100) wafer

Instrument: IONTOF TOF-SIMS.5

Major Species in Spectra: C, H, O, (N)

Minor Species in Spectra: Na, K

Published Spectra: 19

Spectra in Electronic Record: 19

Published Figures: 20

Spectral Category: Reference

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2-deoxy-D-galactose: 1949-89-9, D-galacturonic acid: 91510-52-2, D-glucose: 50-99-7, D-glucuronic acid: 6556-12-3, D-mannose: 3458-28-4, myo-inositol: 87-89-8, L-rhamnose monohydrate: 10030-85-0, D-ribose: 50-69-1, 2-deoxy-D-ribose: 533-67-5, D-xylose: 58-86-6, N-acetyl-D-galactosamine: 1811-31-0, N-acetyl-D-glucosamine: 7512-17-6, N-acetylmuramic acid: 10597-89-4, N-acetylneuraminic acid: 131-48-6

Host Material Characteristics: Homogeneous; solid; single crystal; semiconductor

Chemical Name: D-Allose (01592), L-arabinose (01593), D-fructose (01594), D-fucose (01595), D-galactose (01596), 2-deoxy-D-galactose (01597), D-galacturonic acid (01598), D-glucose (01599), D-glucuronic acid (01600), D-mannose (01601), myo-inositol (01602), L-rhamnose (01603), D-ribose (01604), 2-deoxy-D-ribose (01605), D-xylose (01606), N-acetyl-D-galactosamine (01607), N-acetyl-D-glucosamine (01608), N-acetylmuramic acid (01609), N-acetylneuraminic acid (01610)

Source: Sigma Aldrich and Fluka

Host Composition: $\text{SiO}_2/\text{SiO}_2$

Form: Pure powder dissolved in freshly de-ionized H_2O , sonicated and subsequently drop-deposited on the host wafer

Lot No.: Not specified

Structure: Allose: $\text{C}_6\text{H}_{12}\text{O}_6$, arabinose: $\text{C}_5\text{H}_{10}\text{O}_5$, fructose: $\text{C}_6\text{H}_{12}\text{O}_6$, fucose: $\text{C}_6\text{H}_{12}\text{O}_5$, galactose: $\text{C}_6\text{H}_{12}\text{O}_6$, 2-deoxy-galactose: $\text{C}_6\text{H}_{12}\text{O}_5$, galacturonic acid: $\text{C}_6\text{H}_{10}\text{O}_7$, glucose: $\text{C}_6\text{H}_{12}\text{O}_6$, glucuronic acid: $\text{C}_6\text{H}_{10}\text{O}_7$, mannose: $\text{C}_6\text{H}_{12}\text{O}_6$, myo-inositol: $\text{C}_6\text{H}_{12}\text{O}_6$, rhamnose: $\text{C}_6\text{H}_{12}\text{O}_5$, ribose: $\text{C}_5\text{H}_{10}\text{O}_5$, 2-deoxy-ribose: $\text{C}_5\text{H}_{10}\text{O}_4$, xylose: $\text{C}_5\text{H}_{10}\text{O}_5$, N-acetyl-galactosamine: $\text{C}_8\text{H}_{15}\text{NO}_6$, N-acetylglucosamine: $\text{C}_8\text{H}_{15}\text{NO}_6$, N-acetylmuramic acid: $\text{C}_{11}\text{H}_{19}\text{NO}_8$, N-acetylneuraminic acid: $\text{C}_{11}\text{H}_{19}\text{NO}_9$

History and Significance: As such and/or combined to other small molecules, monosaccharides play various essential roles in the structure and metabolic functions of living organisms.

As Received Condition: Pure powders in glass vials

Analyzed Region: 4–10 randomly selected regions of $200 \times 200 \mu\text{m}^2$

Ex Situ Preparation/Mounting: 50 μl of 0.1M monosaccharide solutions, prepared in freshly de-ionized H_2O , was drop-deposited on $1 \times 1 \text{ cm}^2$ plasma-treated Si (100) substrates, in a fume hood. Full coverage of the solutions on each wafer surface was assured. The samples were left in the fume hood for drying and then directly inserted in the UHV chamber and analyzed.

In Situ Preparation: None

Charge Control: None

Temp. During Analysis: 300 K

Pressure During Analysis: 5.6×10^{-8} Pa

Preanalysis Beam Exposure: None

INSTRUMENT CONFIGURATION

Manufacturer and Model: IONTOF TOF-SIMS.5

Analyzer Type: Time-of-flight

Detector Type: Microchannel plate

Experiment Type: Mass spectra

Sample Rotation: None

Oxygen Flood Source: None

Other Flood Source: None

Unique Instrument Features Used: None

Energy Acceptance Window: 20 eV

Postacceleration Voltage: 10 000 eV

Sample Bias: 0 eV

Specimen Normal-to-analyzer (θ_e): 0°

Ion Sources

Ion Source 1 of 1

Purpose of this Ion Source: Analysis beam

Ion Source Manufacturer: IONTOF (Münster, Germany)

Ion Source Model: 25 keV Bi/Mn emitter

Beam Mass Filter: Electrodynamic mass filter

Beam Species and Charge State: Bi_3^+

Beam Gating Used: None

Additional Beam Comments: None

Beam Voltage: 25 000 eV

Net Beam Voltage (impact voltage): 25 000 eV

Ion Pulse Width: 17.2 ns

Ion Pulse Rate: 10 kHz

Pulsed Beam Current: 0.000 74–0.000 79 nA

Current Measurement Method: Faraday cup

Beam Diameter: N/A (μm)

Beam Raster Size: $200 \times 200 \mu\text{m}^2$

Beam Incident Angle: 45°

Source-to-Analyzer Angle: 45°

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D-ALLOSE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01592	73.028	$C_3H_5O_2^+$	C4 to C6 fragment of M – (H ₂ O)
...	85.028	$C_4H_5O_2^+$	C3 to C6 fragment of M – 2(H ₂ O)
...	97.028	$C_5H_5O_2^+$	C2 to C6 fragment of M – 3(H ₂ O)
...	103.039	$C_4H_7O_3^+$	C3 to C6 fragment of M – (H ₂ O)
...	115.039	$C_5H_7O_3^+$	C2 to C6 fragment of M – 2(H ₂ O)
...	127.039	$C_6H_7O_3^+$	M – 3(H ₂ O) + H
...	145.050	$C_6H_9O_4^+$	M – 2(H ₂ O) + H
...	163.060	$C_6H_{11}O_5^+$	M – (H ₂ O) + H

Accession #:	01592-01
Host Material:	Silicon wafer
Technique:	SIMS
Secondary Source Polarity:	Positive
Mass Range:	0–250 Da
Species Used for Mass Calibration:	CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$
Primary Ion Dose:	$9.71 \times 10^{11} \text{ cm}^{-2}$
Primary Ion Pulse Width:	17.2 ns
Pulsed Beam Current:	0.000 76 nA
Biological Significance:	D-Allose exists only in small amounts in nature

L-ARABINOSE

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01593	73.028	$C_3H_5O_2^+$	C4 to C6 fragment of M – (H ₂ O)
...	85.028	$C_4H_5O_2^+$	C3 to C6 fragment of M – 2(H ₂ O)
...	87.044	$C_4H_7O_2^+$	—
...	89.023	$C_3H_5O_3^+$	C1 to C3 fragment of M + H
...	91.039	$C_3H_7O_3^+$	C3 to C5 fragment of M
...	97.028	$C_5H_5O_2^+$	M – 3(H ₂ O) + H
...	99.044	$C_5H_7O_2^+$	M – 3(H ₂ O) + 3H
...	103.039	$C_4H_7O_3^+$	C1 to C4 fragment of M
...	115.039	$C_5H_7O_3^+$	M – 2(H ₂ O) + H
...	133.050	$C_5H_9O_4^+$	M – (H ₂ O) + H

Accession #:

01593-01

■ Host Material:

Silicon wafer

■ Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–250 Da

Species Used for Mass Calibration:

CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$

Primary Ion Dose:

$9.71 \times 10^{11} \text{ cm}^{-2}$

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

L-Arabinose is found in a range of plant polysaccharides, e.g., the plant cell wall heteropolysaccharides pectin and hemicellulose

D-FRUCTOSE

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01594	73.028	$C_3H_5O_2^+$	C4 to C6 fragment of M – (H ₂ O)
...	85.028	$C_4H_5O_2^+$	C3 to C6 fragment of M – 2(H ₂ O)
...	97.028	$C_5H_5O_2^+$	C2 to C6 fragment of M – 3(H ₂ O)
...	101.023	$C_4H_5O_3^+$	C3 to C6 fragment of M – (H ₂ O) – 2H
...	103.039	$C_4H_7O_3^+$	C3 to C6 fragment of M – (H ₂ O)
...	115.039	$C_5H_7O_3^+$	C2 to C6 fragment of M – 2(H ₂ O)
...	127.039	$C_6H_7O_3^+$	M – 3(H ₂ O) + H
...	145.050	$C_6H_9O_4^+$	M – 2(H ₂ O) + H
...	163.060	$C_6H_{11}O_5^+$	M – (H ₂ O) + H

Accession #:

01594-01

■ Host Material:

Silicon wafer

■ Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–250 Da

Species Used for Mass Calibration:

CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$

Primary Ion Dose:

$9.46 \times 10^{11} \text{ cm}^{-2}$

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 74 nA

Biological Significance:

D-Fructose is important for plant metabolism and energy storage, where, e.g., sucrose (a.k.a. table sugar) is a disaccharide composed of one fructose and one glucose unit. D-Fructose-based polysaccharides, fructans, are important storage macromolecules but also function as cryoprotectants in plants regularly exposed to low temperatures and reduce membrane leakage in periods drought

D-FUCOSE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01595	73.028	$C_3H_5O_2^+$	—
...	75.044	$C_3H_7O_2^+$	C4 to C6 fragment of M
...	85.028	$C_4H_5O_2^+$	—
...	87.044	$C_4H_7O_2^+$	C3 to C6 fragment of M – (H ₂ O)
...	105.018	$C_3H_5O_4^+$	—
...	111.044	$C_6H_7O_2^+$	M – 3(H ₂ O) + H
...	129.055	$C_6H_9O_3^+$	M – 2(H ₂ O) + H
...	147.065	$C_6H_{11}O_4^+$	M – (H ₂ O) + H
...	187.058	$[C_6H_{12}O_5+Na]^+$	M + Na

Accession #:	01595-01
Host Material:	Silicon wafer
Technique:	SIMS
Secondary Source Polarity:	Positive
Mass Range:	0–250 Da
Species Used for Mass Calibration:	CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$
Primary Ion Dose:	$9.71 \times 10^{11} \text{ cm}^{-2}$
Primary Ion Pulse Width:	17.2 ns
Pulsed Beam Current:	0.000 76 nA
Biological Significance:	L-Fucose is found in a wide range of mucoproteins and many membrane glycoproteins and glycolipids (it is, e.g., part of the H-antigen, the base unit of the membrane structure that defines the human blood type).

D-GALACTOSE

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01596	73.028	$C_3H_5O_2^+$	C4 to C6 fragment of M – (H ₂ O)
...	85.028	$C_4H_5O_2^+$	C3 to C6 fragment of M – 2(H ₂ O)
...	91.039	$C_3H_7O_3^+$	C4 to C6 fragment of M
...	97.028	$C_5H_5O_2^+$	C2 to C6 fragment of M – 3(H ₂ O)
...	101.023	$C_4H_5O_3^+$	C3 to C6 fragment of M – (H ₂ O) – 2H
...	103.039	$C_4H_7O_3^+$	C3 to C6 fragment of M – (H ₂ O)
...	115.039	$C_5H_7O_3^+$	C2 to C6 fragment of M – 2(H ₂ O)
...	127.039	$C_6H_7O_3^+$	M – 3(H ₂ O) + H
...	145.050	$C_6H_9O_4^+$	M – 2(H ₂ O) + H
...	163.060	$C_6H_{11}O_5^+$	M – (H ₂ O) + H

Accession #:

01596-01

Host Material:

Silicon wafer

Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–250 Da

Species Used for Mass Calibration:

CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$

Primary Ion Dose:

$9.71 \times 10^{11} \text{ cm}^{-2}$

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

D-Galactose is found in a wide range of glycoproteins and glycolipids and galactose-based polysaccharides occur in certain types of hemicellulose. The milk sugar lactose is a disaccharide composed of one D-galactose and one D-glucose unit

2-DEOXY-D-GALACTOSE

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01597	69.033	$C_4H_5O^+$	—
...	73.028	$C_3H_5O_2^+$	C4 to C6 fragment of M – (H ₂ O)
...	83.049	$C_5H_7O^+$	—
...	85.028	$C_4H_5O_2^+$	C3 to C6 fragment of M – 2(H ₂ O)
...	97.028	$C_5H_5O_2^+$	C2 to C6 fragment of M – 2(H ₂ O) – 2H
...	99.044	$C_5H_7O_2^+$	C2 to C6 fragment of M – 2(H ₂ O)
...	103.039	$C_4H_7O_3^+$	C3 to C6 fragment of M – (H ₂ O)
...	111.044	$C_6H_7O_2^+$	M – 3(H ₂ O) + H
...	125.055	$C_6H_9O_3^+$	M – 2(H ₂ O) + H
...	147.065	$C_6H_{11}O_4^+$	M – (H ₂ O) + H

Accession #:

01597-01

■ Host Material:

Silicon wafer

■ Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–250 Da

Species Used for Mass Calibration:

CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$

Primary Ion Dose:

$9.71 \times 10^{11} \text{ cm}^{-2}$

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

2-Deoxy-D-galactose is not abundant in nature but of scientific relevance as a known inhibitor of membrane glycoprotein synthesis

D-GALACTURONIC ACID

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01598	71.013	$C_3H_3O_2^+$	—
...	73.028	$C_3H_5O_2^+$	—
...	85.028	$C_4H_5O_2^+$	—
...	89.023	$C_3H_5O_3^+$	C1 to C3 fragment of M + H
...	97.028	$C_5H_5O_2^+$	—
...	101.023	$C_4H_5O_3^+$	C1 to C4 fragment of M – (H ₂ O) + H
...	113.023	$C_5H_5O_3^+$	C1 to C5 fragment of M – 2(H ₂ O)
...	131.034	$C_5H_7O_4^+$	C1 to C5 fragment of M – (H ₂ O)
...	141.018	$C_6H_5O_4^+$	M – 3(H ₂ O) + H
...	159.029	$C_6H_7O_5^+$	M – 2(H ₂ O) + H
...	177.039	$C_6H_9O_6^+$	M – (H ₂ O) + H
...	212.076	$[C_6H_{10}O_7+NH_4]^+$	M + NH ₄

Accession #:

01598-01

Host Material:

Silicon wafer

Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–250 Da

Species Used for Mass Calibration:

CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$

Primary Ion Dose:

$9.71 \times 10^{11} \text{ cm}^{-2}$

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

D-Galacturonic acid is the uronic acid of D-galactose and is, among others, the main component of the plant cell wall heteropolysaccharide pectin

D-GLUCOSE

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01599	73.028	$C_3H_5O_2^+$	C4 to C6 fragment of M – (H ₂ O)
...	85.028	$C_4H_5O_2^+$	C3 to C6 fragment of M – 2(H ₂ O)
...	87.044	$C_4H_7O_2^+$	C3 to C6 fragment of M – 2(H ₂ O) + 2H
...	91.039	$C_3H_7O_3^+$	C4 to C6 fragment of M
...	97.028	$C_5H_5O_2^+$	C2 to C6 fragment of M – 3(H ₂ O)
...	103.039	$C_4H_7O_3^+$	C3 to C6 fragment of M – (H ₂ O)
...	115.039	$C_5H_7O_3^+$	C2 to C6 fragment of M – 2(H ₂ O)
...	127.039	$C_6H_7O_3^+$	M – 3(H ₂ O) + H
...	145.050	$C_6H_9O_4^+$	M – 2(H ₂ O) + H
...	163.060	$C_6H_{11}O_5^+$	M – (H ₂ O) + H

Accession #:

01599-01

■ Host Material:

Silicon wafer

■ Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–250 Da

Species Used for Mass Calibration:

CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$

Primary Ion Dose:

$9.71 \times 10^{12} \text{ cm}^{-2}$

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

Glucose is essential for energy storage, energy transport, and cell metabolism in animals, plants, and microorganisms. Glucose is the monomer unit of the polysaccharides starch and glycogen, polymers acting as energy storage in plants and animals, respectively, and the polysaccharide cellulose, which is the main plant cell wall component. Glucose is also part of many di- and oligosaccharides, e.g., sucrose, lactose, and trehalose

D-GLUCURONIC ACID

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01600	71.013	$C_3H_3O_2^+$	—
...	73.028	$C_3H_5O_2^+$	—
...	85.028	$C_4H_5O_2^+$	—
...	89.023	$C_3H_5O_3^+$	C1 to C3 fragment of M + H
...	97.028	$C_5H_5O_2^+$	—
...	99.008	$C_4H_3O_3^+$	C1 to C4 fragment of M – (H ₂ O) – H
...	101.023	$C_4H_5O_3^+$	C1 to C4 fragment of M – (H ₂ O) + H
...	113.023	$C_5H_5O_3^+$	C1 to C5 fragment of M – 2(H ₂ O)
...	117.055	$C_5H_9O_3^+$	—
...	131.034	$C_5H_7O_4^+$	C1 to C5 fragment of M – (H ₂ O)
...	141.018	$C_6H_5O_4^+$	M – 3(H ₂ O) + H
...	159.029	$C_6H_7O_5^+$	M – 2(H ₂ O) + H
...	177.039	$C_6H_9O_6^+$	M – (H ₂ O) + H
...	194.042	$C_6H_{10}O_7^+$	M

Accession #:

01600-01

■ Host Material:

Silicon wafer

■ Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–250 Da

Species Used for Mass Calibration:

CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$

Primary Ion Dose:

$9.71 \times 10^{11} \text{ cm}^{-2}$

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

Glucuronic acid is the uronic acid of D-glucose and plays a major role in the phase II detoxification processes in the liver, where in an enzyme-driven reaction it is bound to toxins to facilitate their excretion

D-MANNOSE

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01601	73.028	$C_3H_5O_2^+$	C4 to C6 fragment of M – (H ₂ O)
...	85.028	$C_4H_5O_2^+$	C3 to C6 fragment of M – 2(H ₂ O)
...	87.044	$C_4H_7O_2^+$	C3 to C6 fragment of M – 2(H ₂ O) + 2H
...	91.039	$C_3H_7O_3^+$	C4 to C6 fragment of M
...	97.028	$C_5H_5O_2^+$	C2 to C6 fragment of M – 3(H ₂ O)
...	103.039	$C_4H_7O_3^+$	C3 to C6 fragment of M – (H ₂ O)
...	115.039	$C_5H_7O_3^+$	C2 to C6 fragment of M – 2(H ₂ O)
...	127.039	$C_6H_7O_3^+$	M – 3(H ₂ O) + H
...	145.050	$C_6H_9O_4^+$	M – 2(H ₂ O) + H
...	163.060	$C_6H_{11}O_5^+$	M – (H ₂ O) + H

Accession #:

01601-01

Host Material:

Silicon wafer

Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–250 Da

Species Used for Mass Calibration:

CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$

Primary Ion Dose:

$9.71 \times 10^{11} \text{ cm}^{-2}$

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

D-mannose is part of the glycosylation process of certain glycoproteins. During the C-mannosylation process, a mannose monosaccharide attaches by covalent bond formation to tryptophan

MYO-INOSITOL

Spectrum ID #	Mass(Da)	Species	Peak Assignment
01602	73.028	$C_3H_5O_2^+$	C4 to C6 fragment of M – (H ₂ O)
...	85.028	$C_4H_5O_2^+$	C3 to C6 fragment of M – 2(H ₂ O)
...	102.031	$C_4H_6O_3^+$	M – C ₂ H ₄ O ₂ ring fragment – (H ₂ O)
...	109.028	$C_6H_5O_2^+$	M – 4(H ₂ O) + H
...	127.039	$C_6H_7O_3^+$	M – 3(H ₂ O) + H
...	145.050	$C_6H_9O_4^+$	M – 2(H ₂ O) + H
...	163.060	$C_6H_{11}O_5^+$	M – (H ₂ O) + H
...	181.071	$C_6H_{13}O_6^+$	M + H

Accession #:

01602-01

■ Host Material:

Silicon wafer

■ Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–250 Da

Species Used for Mass Calibration:

CH₂⁺, CH₃⁺, C₂H₄⁺, C₃H₆⁺, C₂H₄O⁺

Primary Ion Dose:

9.71 × 10¹¹ cm⁻²

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

Myo-inositol derivatives serve as a Ca²⁺ secondary messenger; myo-inositol is also the basis for the phosphate storing molecule phytic acid in certain plants as well as the component of a wide range of phospholipids

L-RHAMNOSE

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01603	71.049	$C_4H_7O^+$	—
...	73.028	$C_3H_5O_2^+$	—
...	75.044	$C_3H_7O_2^+$	C4 to C6 fragment of M
...	85.028	$C_4H_5O_2^+$	—
...	87.044	$C_4H_7O_2^+$	C3 to C6 fragment of M – (H ₂ O)
...	89.023	$C_3H_5O_3^+$	—
...	99.044	$C_5H_7O_2^+$	C2 to C6 fragment of M – 2(H ₂ O)
...	101.060	$C_5H_9O_2^+$	C2 to C6 fragment of M – 2(H ₂ O) + 2H
...	103.039	$C_4H_7O_3^+$	—
...	111.044	$C_6H_7O_2^+$	M – 3(H ₂ O) + H
...	129.055	$C_6H_9O_3^+$	M – 2(H ₂ O) + H
...	147.065	$C_6H_{11}O_4^+$	M – (H ₂ O) + H
...	187.058	$[C_6H_{12}O_5+Na]^+$	M + Na

Accession #:

01603-01

■ Host Material:

Silicon wafer

■ Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–250 Da

Species Used for Mass Calibration:

CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$

Primary Ion Dose:

$9.71 \times 10^{11} \text{ cm}^{-2}$

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

L-Rhamnose is a component of the rhamnogalacturonan pectins as well as of certain bacterial outer cell membranes

D-RIBOSE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01604	73.028	$C_3H_5O_2^+$	C3 to C5 fragment of M – (H ₂ O)
...	85.028	$C_4H_5O_2^+$	C4 to C5 fragment of M – 2(H ₂ O)
...	89.023	$C_3H_5O_3^+$	C1 to C3 fragment of M + H
...	97.028	$C_5H_5O_2^+$	M – 3(H ₂ O) + H
...	115.039	$C_5H_7O_3^+$	M – 2(H ₂ O) + H
...	133.050	$C_5H_9O_4^+$	M – (H ₂ O) + H

Accession #:	01604-01
Host Material:	Silicon wafer
Technique:	SIMS
Secondary Source Polarity:	Positive
Mass Range:	0–250 Da
Species Used for Mass Calibration:	CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$
Primary Ion Dose:	$9.71 \times 10^{11} \text{ cm}^{-2}$
Primary Ion Pulse Width:	17.2 ns
Pulsed Beam Current:	0.000 76 nA
Biological Significance:	D-Ribose (as α-D-ribofuranose) forms the backbone of RNA and is, among others, part of the molecules ATP (adenosine triphosphate), ADP (adenosine diphosphate), and NAD (nicotinamide adenine dinucleotide) essential for the metabolism of all living cells

2-DEOXY-D-RIBOSE

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01605	57.033	$C_3H_5O^+$	—
...	69.033	$C_4H_5O^+$	—
...	73.065	$C_4H_9O^+$	—
...	81.033	$C_5H_5O^+$	$M - 3(H_2O) + H$
...	99.044	$C_5H_7O_2^+$	$M - 2(H_2O) + H$
...	117.06	$C_5H_9O_3^+$	$M - (H_2O) + H$

Accession #:

01605-01

Host Material:

Silicon wafer

Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–250 Da

Species Used for Mass Calibration:

CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$

Primary Ion Dose:

$9.71 \times 10^{11} \text{ cm}^{-2}$

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

2-Deoxy-D-ribose forms the backbone of DNA

D-XYLOSE			
Spectrum ID #	Mass (Da)	Species	Peak Assignment
01606	73.028	$C_3H_5O_2^+$	C3 to C5 fragment of M – (H ₂ O)
...	85.028	$C_4H_5O_2^+$	C4 to C5 fragment of M – 2(H ₂ O)
...	97.028	$C_5H_5O_2^+$	M – 3(H ₂ O) + H
...	115.039	$C_5H_7O_3^+$	M – 2(H ₂ O) + H
...	133.050	$C_5H_9O_4^+$	M – (H ₂ O) + H

Accession #:	01606-01
Host Material:	Silicon wafer
Technique:	SIMS
Secondary Source Polarity:	Positive
Mass Range:	0–250 Da
Species Used for Mass Calibration:	CH_2^+ , CH_3^+ , $C_2H_4^+$, $C_3H_6^+$, $C_2H_4O^+$
Primary Ion Dose:	$9.71 \times 10^{11} \text{ cm}^{-2}$
Primary Ion Pulse Width:	17.2 ns
Pulsed Beam Current:	0.000 76 nA
Biological Significance:	D-Xylose is the main component of xylan, a highly abundant hemicellulose, and is, among others, also found as residue in certain types of pectin

N-ACETYL-D-GALACTOSAMINE

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01607	60.044	C ₂ H ₆ NO ⁺	Amide group
...	72.044	C ₃ H ₆ NO ⁺	C2 + amide group
...	84.044	C ₄ H ₆ NO ⁺	—
...	100.039	C ₄ H ₆ NO ₂ ⁺	—
...	114.055	C ₅ H ₈ NO ₂ ⁺	—
...	126.055	C ₆ H ₈ NO ₂ ⁺	M – 3(H ₂ O) – (C ₂ H ₃ O) at amide group + 2H
...	138.055	C ₇ H ₈ NO ₂ ⁺	M – 3(H ₂ O) – C6 containing side group + 2H
...	144.066	C ₆ H ₁₀ NO ₃ ⁺	M – 2(H ₂ O) – (C ₂ H ₃ O) at amide group + 2H
...	162.076	C ₆ H ₁₂ NO ₄ ⁺	M – (H ₂ O) – (C ₂ H ₃ O) at amide group + 2H
...	186.076	C ₈ H ₁₂ NO ₄ ⁺	M – 2(H ₂ O) + H
...	204.087	C ₈ H ₁₄ NO ₅ ⁺	M – (H ₂ O) + H
...	222.097	C ₈ H ₁₆ NO ₆ ⁺	M + H

Accession #:

01607-01

Host Material:

Silicon wafer

Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–250 Da

Species Used for Mass Calibration:

CH₂⁺, CH₃⁺, C₂H₄O⁺, C₈H₁₆NO₆⁺

Primary Ion Dose:

9.71 × 10¹¹ cm⁻²

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

N-acetylgalactosamine is found in a wide range of mucoproteins where it often serves as a linking point between the protein backbone and its covalently attached polysaccharide chains

N-ACETYL-D-GLUCOSAMINE

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01608	60.044	C ₂ H ₆ NO ⁺	Amide group
...	72.044	C ₃ H ₆ NO ⁺	C2 + amide group
...	84.044	C ₄ H ₆ NO ⁺	—
...	100.039	C ₄ H ₆ NO ₂ ⁺	—
...	114.055	C ₅ H ₈ NO ₂ ⁺	—
...	126.055	C ₆ H ₈ NO ₂ ⁺	M – 3(H ₂ O) – (C ₂ H ₃ O) at amide group + 2H
...	138.055	C ₇ H ₈ NO ₂ ⁺	M – 3(H ₂ O) – C6 containing side group + 2H
...	144.066	C ₆ H ₁₀ NO ₃ ⁺	M – 2(H ₂ O) – (C ₂ H ₃ O) at amide group + 2H
...	162.076	C ₆ H ₁₂ NO ₄ ⁺	M – (H ₂ O) – (C ₂ H ₃ O) at amide group + 2H
...	186.076	C ₈ H ₁₂ NO ₄ ⁺	M – 2(H ₂ O) + H
...	204.087	C ₈ H ₁₄ NO ₅ ⁺	M – (H ₂ O) + H
...	222.097	C ₈ H ₁₆ NO ₆ ⁺	M + H

Accession #:

01608-01

■ Host Material:

Silicon wafer

■ Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–250 Da

Species Used for Mass Calibration:

CH₂⁺, CH₃⁺, C₂H₄O⁺, C₈H₁₆NO₆⁺

Primary Ion Dose:

9.71*10¹¹ cm⁻²

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

N-acetyl-D-glucosamine is the monomer unit of chitin, a polysaccharide that is, among others, the primary components of arthropodal exoskeletons and fungal cell walls. Independently, alternating covalently bound *N*-acetyl-D-glucosamine and *N*-acetylmuramic acid units form the amino sugar chains in the peptidoglycan, the bacterial cell wall. *N*-acetyl-D-glucosamine is also found, among others, in mucoproteins

N-ACETYL-MURAMIC ACID

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01609	60.044	C ₂ H ₆ NO ⁺	Amide group
...	72.044	C ₃ H ₆ NO ⁺	C2 + amide group
...	84.044	C ₄ H ₆ NO ⁺	—
...	98.060	C ₅ H ₈ NO ⁺	—
...	100.039	C ₄ H ₆ NO ₂ ⁺	—
...	114.055	C ₅ H ₈ NO ₂ ⁺	—
...	126.055	C ₆ H ₈ NO ₂ ⁺	—
...	138.055	C ₇ H ₈ NO ₂ ⁺	—
...	144.066	C ₆ H ₁₀ NO ₃ ⁺	—
...	186.076	C ₈ H ₁₂ NO ₄ ⁺	—
...	252.108	C ₉ H ₁₈ NO ₇ ⁺	M – (C ₂ H ₃ O) at amide group + 2H
...	276.108	C ₁₁ H ₁₈ NO ₇ ⁺	M – (H ₂ O) + H
...	294.118	C ₁₁ H ₂₀ NO ₈ ⁺	M + H

Accession #:

01609-01

Host Material:

Silicon wafer

Technique:

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–300 Da

Species Used for Mass Calibration:

CH₂⁺, CH₃⁺, C₂H₄O⁺, C₁₁H₂₀NO₈⁺

Primary Ion Dose:

9.71 × 10¹¹ cm⁻²

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

Alternating covalently bound *N*-acetylmuramic acid and *N*-acetyl-D-glucosamine units form the amino sugar chains of the peptidoglycan, the bacterial cell wall

N-ACETYLNEURAMINIC ACID

Spectrum ID #	Mass (Da)	Species	Peak Assignment
01610	60.044	C ₂ H ₆ NO ⁺	Amide group
...	72.044	C ₃ H ₆ NO ⁺	C2 + amide group
...	84.044	C ₄ H ₆ NO ⁺	—
...	127.075	C ₇ H ₁₁ O ₂ ⁺	—
...	274.092	C ₁₁ H ₁₆ NO ₇ ⁺	M – 2(H ₂ O) + H
...	292.103	C ₁₁ H ₁₈ NO ₈ ⁺	M – (H ₂ O) + H
...	310.113	C ₁₁ H ₂₀ NO ₉ ⁺	M + H

Accession #:

01610-01

■ **Host Material:**

Silicon wafer

■ **Technique:**

SIMS

Secondary Source Polarity:

Positive

Mass Range:

0–315 Da

Species Used for Mass Calibration:

CH₂⁺, CH₃⁺, C₂H₄O⁺, C₁₁H₂₀NO₉⁺

Primary Ion Dose:

9.71 × 10¹¹ cm⁻²

Primary Ion Pulse Width:

17.2 ns

Pulsed Beam Current:

0.000 76 nA

Biological Significance:

N-acetylneuraminic acid is found in a wide range of glycoproteins and is crucial in the modulation of neurosynaptic transmission in humans

EXPANDED $[M - OH]^+$ AND $[M + H]^+$ PEAKS FOR SPECTRA OF STANDARD AND AMINO-MONOSACCHARIDES, RESPECTIVELY

Accession #: [01592-01](#), [01593-01](#), [01594-01](#), [01595-01](#), [01596-01](#), [01597-01](#), [01598-01](#), [01599-01](#), [01600-01](#), [01601-01](#), [01602-01](#), [01603-01](#), [01604-01](#), [01605-01](#), [01606-01](#), [01607-01](#), [01608-01](#), [01609-01](#), [01610-01](#)