ANALYSIS OF CARBOHYDRATES AND GLYCOCONJUGATES BY MATRIX-ASSISTED LASER DESORPTION/IONIZATION MASS SPECTROMETRY: AN UPDATE FOR 2009–2010

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This review is the sixth update of the original article published in 1999 on the application of MALDI mass spectrometry to the analysis of carbohydrates and glycoconjugates and brings coverage of the literature to the end of 2010. General aspects such as theory of the MALDI process, matrices, derivatization, MALDI imaging, arrays and fragmentation are covered in the first part of the review and applications to various structural typed constitutes the remainder. The main groups of compound that are discussed in this section are oligo and polysaccharides, glycoproteins, glycolipids, glycosides and biopharmaceuticals. Many of these applications are presented in tabular form. Also discussed are medical and industrial applications of the technique, studies of enzyme reactions and applications to chemical synthesis. © 2014 Wiley Periodicals, Inc. Mass Spec Rev 34:268–422, 2015

Keywords: *MALDI; carbohydrates; glycoproteins; glycolipids; biopharmaceuticals*

I. INTRODUCTION

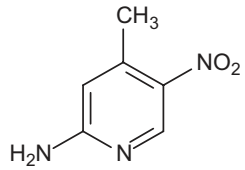
This review is a continuation of the six earlier ones in this series (Harvey, 1999, 2006, 2008, 2009, 2011, 2012) on the application of matrix-assisted laser desorption/ionization mass spectrometry (MALDI) mass spectrometry (MS) to the analysis of carbohydrates and glycoconjugates. It is intended to bring the coverage of the literature to the end of 2010. Although the intention is to be a comprehensive as possible, there is an increasing tendency to publish MALDI data in Supplementary information. Because of the ever-increasing number of papers and journals, it has not been possible to check all supplementary information and, consequently, papers that do not refer to MALDI in the main text may well have been omitted. Also omitted are papers that simply report the mass of glycoproteins and those concerned with nucleotides and nucleosides: the latter compounds, although containing carbohydrates are considered to be different types of compound.

MALDI continues to be a major technique for the analysis of carbohydrates; Figure 1 shows the year-by-year increase in papers reporting use of the technique for the period 1991–2010. Because the review is designed to complement the earlier work, structural formulae, etc. that were presented earlier are not repeated. However, a citation to the structure in the earlier works is indicated by its number with a prefix designating the review containing the structure (i.e., **1/x** refers to structure **x** in the first review and **2/x** to a structure in the second). A large number of books and review articles directly concerned with, or including MALDI analysis of carbohydrates and glycoconjugates, have been published during the review period. Those of a general nature are listed in Table 1; those concerned with specific carbohydrate types are listed in the appropriate sections.

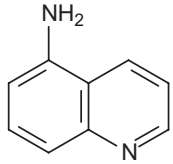
II. THEORY

Details of the MALDI process are still not fully understood and several investigators have attempted to obtain greater understanding. Although not all of these studied have involved carbohydrates, they are included here because MALDI processes for different compounds are likely to be similar.

One of the commonly accepted models for the formation of analyte ions in MALDI-MS assumes a primary ionization of the matrix, for example, by photoionization leading, among other things, to stable protonated and deprotonated matrix ions. Peptide and protein ions are then envisaged as being formed by secondary proton transfer reactions in the expanding matrix plume. This model has been checked experimentally by Hillenkamp et al. (2009) by comparing the yield of positive to negative ions of three peptides (bradykinin, angiotensin I and fibrinopeptide A) and six matrices α-cyano-4-hydroxycinnamic acid (CHCA, **1/23**), 2,5-dihydroxybenzoic acid (DHB, **1/26**), 6-azo-2-thiothymine (ATT, **1/45**), 4-nitroaniline (4-NA, **3/3**), 2-amino-5-nitro-4-picoline (ANP, **1**) and 5-aminoquinoline (5-AQ, **2**), differing in gas-phase basicity by about 100 kJ/mol. It was shown that the observed ion yields cannot be explained by any single and consistent set of parameters such as gas-phase basicity or acidity of the analyte and matrix. It was concluded that the existing simple model needs be modified to fully explain the experimental findings.



2-Amino-5-nitro-4-picoline, **1**



5-Aminoquinoline, **2**

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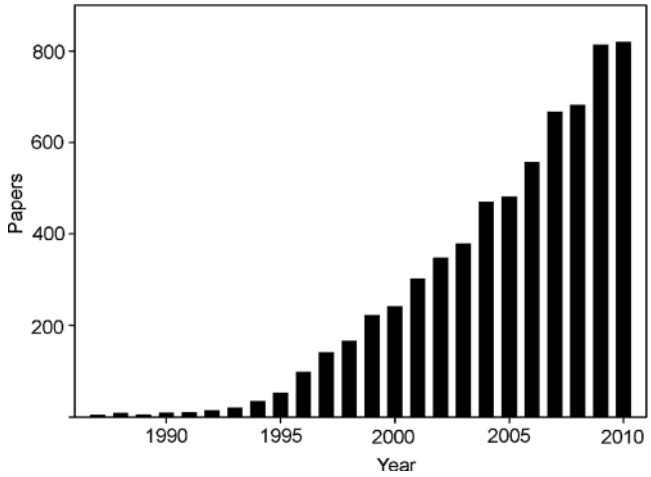


FIGURE 1. Papers reporting the use of MALDI MS for the analysis of carbohydrates and glycoconjugates by year.

Liu et al. (2009a) have used synchronized dual-polarity MALDI MS to demonstrate incoherent production of positive and negative matrix ions. In both positive and negative ion modes, matrix ions were found to appear from thin, homogeneous DHB matrix films at different threshold laser fluences. The presence of singly charged molecular matrix ions suggests that the existence of DHB ion-pairs may not be a prerequisite in the MALDI process. Photoelectrons induced by the laser excitation may assist the production of negative DHB ions, as shown in experiments conducted with stainless steel and glass substrates. At high laser fluences, the relative yield of positive and negative matrix ions remained constant when homogeneous matrix films were used, but the yield fluctuated significantly with inhomogeneous crystal morphology. This result was also inconsistent with the hypothesis that matrix ion-pairs are essential primary ions. Thus, results from both low and high laser fluences suggest that the production of positive and negative matrix ions in MALDI may occur *via* independent pathways.

The same authors (Liu et al., 2010a) have examined the initial ionization reaction in MALDI based on the appearance of photoelectrons. The threshold laser fluence for the ejection of photoelectrons from DHB, sinapinic acid (**1/48**) and 2,4,6-trihydroxyacetophenone (THAP, **1/44**) on stainless steel targets was found to be 0.05, 0.41, and 8.39 mJ/cm^2, respectively. These values were considerably lower than those for MALDI ions, indicating that the electron detachment probably precedes other ionization reactions. The stainless steel target was thought to

TABLE 1. General Reviews to the Analysis of Carbohydrates With Specific Reference to MALDI Analysis

Subject	Comments	Citations	Reference
General review on carbohydrate analysis by ESI and MALDI	Theory, EI, FAB, ESI, MALDI. Application to carbohydrate types	358	(Harvey, 2010)
MALDI MS - Applications in carbohydrate analysis	Short review. In Chinese. Not on-line	-	(Hongmin et al., 2009)
MALDI ionization mechanisms	Discusses most aspects of current thinking on the MALDI process	237	(Knochenmuss, 2010)
Sulfated oligosaccharides - new targets for drug development	New approaches for detection and analysis of sulfated oligosaccharides	-	(Kovensky, 2009)
Use of ionic liquids, including use as matrices	Use in sample preparation and as MALDI matrices	148	(Liu, et al., 2009e)
Coupling of planar chromatography to mass spectrometry	Good general review (no specific mention of carbohydrates)	118	(Morlock & Schwack, 2010)
Development of MALDI ion sources	General review and coupling to chromatographic systems	126	(O'Connor, 2010)
Quantitative glycomics	Mainly glycans from glycoproteins	35	(Orlando, 2010)
Off-line coupling of microcolumn separations to desorption mass spectrometry	Mainly proteins. Some glycoproteins. Table of applications	204	(Peš & Preisler, 2010)
Oligosaccharide analysis by graphitized carbon LC/MS	Includes table with applications to MALDI	76	(Ruhaak et al., 2009)
TLC/HPTLC with direct MS detection, 5-Year review	General review with a section on glycolipids	-	(Schiller et al., 2010)
Glycan analysis by mass spectrometry	Short review, MALDI and ESI, applications to *N*-linked glycans	20	(Sekiya & Iida, 2008)
Deciphering carbohydrate structures by ion mobility MS	Short general review of glycomics and ion mobility. Applications to flavonoids, GAGs and glycoproteins	96	(Vakhrushev & Peter- Katalinić, 2010)
Modern MALDI-TOF mass spectrometry	Development of TOF mass spectrometers since the introduction of MALDI	26	(Vestal, 2009)
MALDI Mass spectrometry of carbohydrates	Short general review (In Chinese)	-	(Wang et al., 2009f)

play an insignificant role in the production of photoelectrons because suspended DHB produced a photoelectron signal similar to DHB on the surface. In addition, decreasing the DHB thickness on the target reduced the photoelectron intensity. For crystalline DHB and sinapinic acid, the photoelectron intensity was found to increase with the laser fluence (nitrogen laser at 337 nm) in less than a second order relationship, suggesting considerable reductions of ionization potentials in comparison with free molecules. According to *ab initio* calculations, the ionization potential of DHB clusters was found to reduce as the cluster size increased from monomer to octamer. The paper discusses the impact of these abundant electrons on ion production in MALDI.

The earlier rate equation model for MALDI ion formation and reaction (Knochenmuss, 2002, 2003), has been extended to include positive and negative ions of both matrix and analyte (Knochenmuss, 2009). The resulting positive/negative ratios of secondary analyte ions show that a recent static equilibrium approach is not adequate for quantitative analysis of MALDI experiments. Although the ion ratios remain close to unity whenever the reaction free energies are at least moderately favorable, deviations from this condition result in unequal ratios of oppositely charged ions and show once again that the dynamic aspects of MALDI cannot be neglected.

Molecular dynamics simulations of MALDI have been performed to investigate laser pulse width and fluence effects on primary and secondary ionization process. At the same fluence, short (35 or 350 psec) pulses were found to give much higher initial pressures and ion concentrations than longer ones (3 ns). These differences were found not to persist because the system relaxes towards local thermal equilibrium on a nanosecond timescale. Higher fluences were found to accentuate the initial disparities. Axial velocities of ions and neutrals were found to span a wide range and to be fluence-dependent. The total ion yield was found to be only weakly dependent on the pulse width and to be consistent with experimental estimates. Secondary reactions of matrix cations with analyte neutrals were efficient even though analyte ions were ablated in clusters of matrix (Knochenmuss & Zhigilei, 2010).

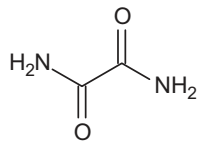
Lai et al. (2010) have employed transition state theory for modeling the desorption of surface ions, assuming chemical and thermal equilibrium in the solid state prior to desorption. The method was different from the use of conventional models that assume chemical equilibrium in the gas phase. This solid-state thermodynamic interpretation was used to examine the desorption of THAP and of an angiotensin I/THAP mixture. It successfully described the changes in ion yield with the effective temperature under various laser fluence and initial temperature conditions. The analysis also revealed the key role played by ion concentration in the modeling used to provide the best fit of the model to observations. Divergence of the ion beam with laser fluence was also examined using an imaging detection method and the signal saturation normally seen at high fluence was appropriately reduced by ion focusing. Simplified but deceptive theoretical interpretations were obtained when the analysis was conducted without adequate calibration of the instrument bias.

The laser plume produced by several ionic liquid matrices has been studied by a post-ionization approach in which the neutrals in the ablation plume were ionized with a second laser pulse. It was found that after the initial event that produced the ions, a second, time-delayed, ablation event occurred in which the plume contained only neutral molecules. The presence of these neutral molecules was explained by a reflected-shockwave model in which the shockwave emerging from the laser ablation is reflected from the sample plate behind the sample. It was assumed that when the shockwave arrived at the sample surface it caused a second ablation of the neutral molecules (Hellwig et al., 2009).

The 355 nm multiphoton dissociation and ionization of 2,5-dihydroxyacetophenone (DHAP, **1/43**) has been studied (Dyakov et al., 2009). The experimental results indicate that photoionization that occurs in the gas phase after DHAP vaporizes from the solid phase may not play an important role in the MALDI process.

III. INSTRUMENTATION

A combined IR-MALDI ion source with an electrospray ionization (ESI) emitter for post desorption ionization has been described (Sampson, Murray, & Muddiman, 2009). The source produced multiply charged ions from proteins but singly charged ions from carbohydrates (*O*-glycans cleaved from mucin (MUC) were tested) and avoided the fragmentation produced by some other techniques. IR-MALDI MS with a laser emission in the 6 μm wavelength range, which utilized energy absorption at the CO double-bond stretch region, has been investigated for analysis of several types of biomolecule. The softness of IR-MALDI MS was evident in the negative ion mode where abundant $[M-H]^-$ ions were obtained for acidic biomolecules with sulfate, phosphate, or carboxylate groups. Better sensitivity was obtained than with ultraviolet (UV) MALDI MS. Furthermore, there was no substantial loss of sialic acid due to the prompt fragmentation from sialylated glycoconjugates such as gangliosides. Such loss is a common problem with MALDI analysis of sialylated carbohydrates. The technique was used in conjunction with a potent new matrix, oxamide (**3**), resulting in the use of low laser fluence, and removing one of the limitations of MALDI MS for biomolecular analysis of UV-MALDI-sensitive molecules (Tajiri, Takeuchi, & Wada, 2009a).



Oxamide, **3**

Tu and Gross (2009) have reviewed methods for miniaturizing sample spots for MALDI analysis. Topics include minimizing sample dispersion by target modification, the use of hydrophobic materials as MALDI-plate surfaces, the use of microdispensing devices such as piezoelectric dispensers and the use of droplet charging by induction or polarization. A simple device for MALDI sample preparation, based on the spraying of matrix/sample solution through a stainless steel sieve, has been used for the preparation of MALDI samples of peptides, polysaccharides (PSs) and high molecular weight (MW) proteins (Cristoni et al., 2009). The spectra obtained by laser irradiation of the resulting microspots exhibit resolution and sensitivity higher than those achieved by the commonly employed dried droplets method. Furthermore, the target surface

was more homogeneous than those obtained by the dried droplet method. CHCA and super-DHB (DHB + 2-OH,5-OMe-benzoic acid) (s-DHB) matrices were used and applications were to insulin and dextran oligomers.

Ultrasound produced by a simple piezoelectric device has been used as an alternative method for soft ionization of biomolecules. Cavitation was proposed as the major mechanism producing the ions and the technique was applied to carbohydrates, proteins and fatty acids. However, although an abundant ion, said to be the $[M+H]^+$ from the high-mannose glycan $Man_8GlcNAc_2$ (**5/20**), was obtained in the presence of DHB, THAP, or sinapinic acid, neither the mass nor the stated elemental composition were consistent with this structure (Wu et al., 2010a).

A. Ion Mobility Mass Spectrometry

The recent availability of commercial ion mobility instruments offers another dimension to carbohydrate analysis by providing the ability to separate by molecular shape and offering the possibility of rapid isomer differentiation. However, resolutions on current instruments are comparatively poor and do not match those that can be obtained with high performance liquid chromatography (HPLC). A comparison of three types of ion mobility MS (field asymmetric waveform ion mobility (FAIMS), drift tube and traveling wave ion mobility spectrometry (TWIMS)) for separation of chiral molecules with applications to monosaccharides has been reported (Enders & McLean, 2009). Data are best reported as rotationally averaged collisional cross-sections. These can be obtained directly with drift tubes and indirectly with the TWIMS instruments. Obtaining such measurements with FAIMS instruments, however, is more challenging.

Collisional-cross sections have been measured for a large number of biologically relevant molecules including oligonucleotides ($n = 96$), carbohydrates ($n = 192$), lipids ($n = 53$), and peptides ($n = 610$). Collisional cross sections increased with mass but were found to be different for each molecular type in the order oligonucleotides < carbohydrates < peptides < lipids. The specific correlations were best described by logarithmic regressions. Thus, the technique was able to separate compounds of different structures but with the same or similar MWs. In addition, some separation of compounds with the same mass within a particular class was possible. The latter point was demonstrated by separations of isobaric oligonucleotides, which were interpreted by molecular dynamics simulations (Fenn et al., 2009; McLean, 2009).

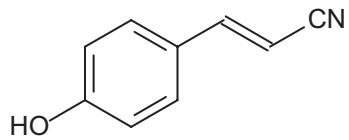
Fenn and McLean (2009) have used ion mobility to extract carbohydrate ions from incubation mixtures obtained from protein-*N*-glycosidase (PNGase) F release of *N*-glycans. Glycoproteins such as ribonuclease B (RNaseB) were first digested with trypsin followed by PNGase F and then analyzed directly by ion mobility MS with a Waters Synapt instrument. The carbohydrate ions showed different mobilities from peptide and other contaminating ions allowing them to be extracted directly from the crude mixtures. Both ESI and MALDI ion sources were used; the MALDI ion source was better at ionizing the larger carbohydrates and did not suffer from the problem of producing both $[M+H]^+$ and $[M+Na]^+$ ions that were seen in the ESI source. The technique would appear to have great potential for rapid glycan analysis, particularly as the Synapt instrument also offers the ability to fragment the isolated ions.

IV. MATRICES

Hossain and Limbach (2010) have reviewed matrices used for MALDI analysis of several compound classed including carbohydrates. The review covers common matrices such as DHB and CHCA and less common systems such as liquid matrices and carbon nanotubes (138 references). The use of ionic liquid matrices has also been included in a review by Liu et al. (2009e) although the bulk of this review discusses the use of ionic liquids for sample preparation.

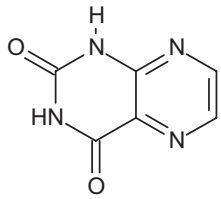
A. Common Matrices

The thermal stability of several commonly used crystalline matrices, 2,5-DHB, THAP, CHCA, sinapinic acid, *nor*-harmane (**1/35**) and harmane (**1/34**) has been studied by heating them at their melting point and characterizing the remaining material by a variety of spectroscopic and chromatographic techniques. In general, all compounds, except for CHCA and sinapinic acid, remained unchanged after fusion. CHCA showed loss of CO_2, yielding a *trans*-/*cis*-4-hydroxyphenylacrylonitrile (**4**) mixture. Sinapinic acid showed mainly *cis*- to-*trans* thermal isomerization and, with very poor yield, loss of CO_2 (Tarzi, Nonami, & Erra-Balsells, 2009).



4-Hydroxyphenylacrylonitrile, **4**

1H-Pteridine-2,4-dione (lumazine, **5**) has been described as a good matrix for phospholipids where the presence of cation-containing compounds suppresses signals from neutral compounds. Phosphatidyinositol was reported to give a signal that was an order of magnitude higher than that obtained from DHB (Calvano, Carulli, & Palmisano, 2010).



1H-Pteridine-2,4-dione (lumazine), **5**

B. Matrices for Low-Mass Compounds

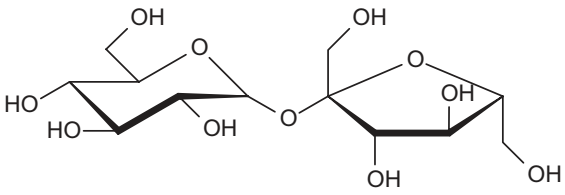
1. Nanoparticles

A number of papers have reported the use of various nanoparticles as matrices. Unlike traditional chemical matrices, these materials generally produced little or no signal in the low mass

region, thus making them ideal for analysis of small carbohydrates.

Titanium dioxide micro- and nano-particles, prepared by hydrolysis of Ti butoxide and maintained in aqueous solution, have been evaluated as matrices for the detection of several small molecules. Most of the reported applications were to lipids but the nanoparticles were also applied to flavonols/anthocyanins and their glycosides in rose petals. The spectra showed ions from many more small molecules than did spectra recorded from DHB, particularly in the region of the DHB matrix ions. One advantage of the nanoparticles is that their small size (average of about 200 nm) facilitates their penetration into tissue for *in situ* imaging (Lorkiewicz & Yappert, 2009). Titanium dioxide (TiO_2) has also be used by Kawasaki, Okamura, and Arakawa (2010) for ionization of several types of compound, including carbohydrates, with a similar absence of low mass matrix ions. In a study of the most suitable crystalline form, the anatase-type TiO_2, was shown to be the best.

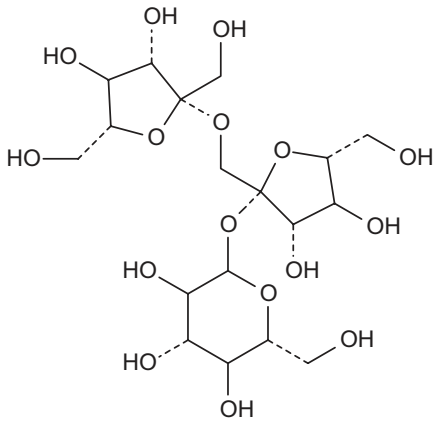
Nanoparticles of diamond, TiO_2, titanium silicon oxide, barium strontium titanium oxide, and silver have been examined for their potential as MALDI matrices for direct laser desorption/ionization of carbohydrates, especially fructans, from plant tissue. Two sample preparation methods including solvent-assisted and solvent-free (dry) deposition were compared. All examined nanoparticles except Ag were found to desorb/ionize standard sucrose (**6**) and fructans in both positive and in negative ion mode. In positive ion mode, sugars gave $[M+Na]^+$ and/or $[M+K]^+$ ions depending on the ionic composition of the sample spot, and $[M-H]^-$ ions in negative mode. Ag nanoparticles yielded good signals only for non-salt doped samples that were measured in the negative ion mode. When used to study fructans in plant tissues all the nanoparticles except Ag could desorb/ionize carbohydrates in both ion modes. nanoparticles gave similar limit of detection (LOD) for standard fructan triose (1-kestose, **7**) in the positive ion mode and better LODs in the negative ion mode than those given by the common crystalline organic MALDI matrices such as DHB, *nor*-harmane or carbon nanotubes. Although lower signal-to-noise ratio (*S*/*N*) signals were obtained from the tissues with solvent-free matrix deposition than when solvent was used, the reproducibility averaged over all sample was more uniform (Gholipour et al., 2010).



Sucrose, **6**

MALDI detection at the level of several hundred zmoles has been achieved by the addition of gold nanoparticles (AuNPs) with a diameter of several tens of nanometers into a sample solution (Shibamoto et al., 2009). *N*-Acetyl-tetraose 1 fmol/μL gave a strong signal in the presence of 50 nm AuNP (4.5×10^7 particles). The mechanism appears to be related to surface plasmon (SP) excitation of the AuNPs.

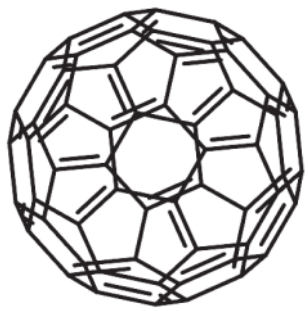
Citrate-capped AuNPs have been shown to act as matrices for the determination of several types of biomolecule, including



1-Kestose, **7**

carbohydrates such as starch, dextrins, and glycosphingolipids (GSLs) in the presence of high concentrations of salt (Wuhrer, Koeleman, & Deelder, 2009b). With the GSLs, however, some loss of sialic acid (**1/11**) was found.

A combination of immobilized silica and DHB on iron oxide magnetic nanoparticles has been shown to give a clean background and to be appropriate for the analysis of a range of small molecules, including glycolipids (Tseng et al., 2010). The ratio between SiO_2 and DHB was found to affect the surface immobilization of DHB on the nanoparticle, critically controlling the ionization efficiency and background. Enhancements of molecular ion signal over those produced from DHB alone were noted and high quality product-ion spectra were obtained. Fullerene (**8**)-derivatized silica (pore size 30 nm) also appears to be good for small molecules including monosaccharides (Szabo et al., 2010b).

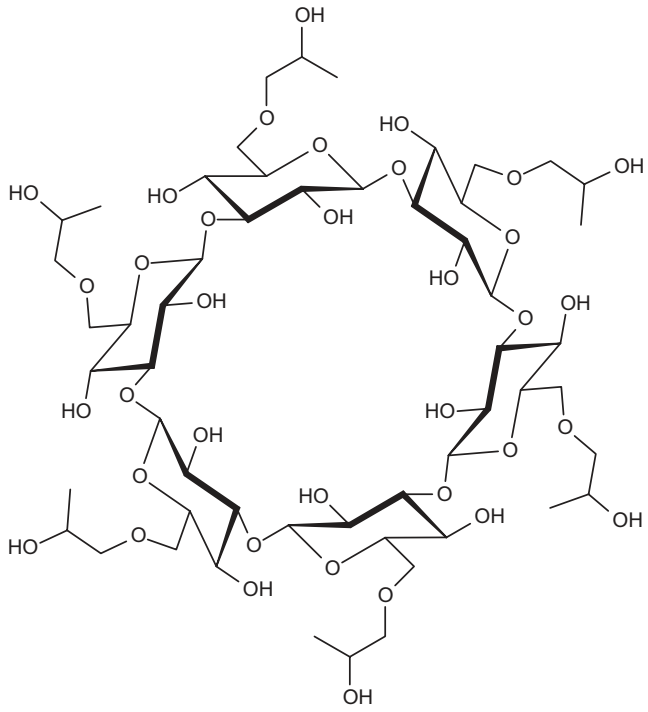


Fullerene, **8**

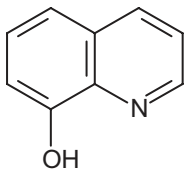
Multifunctional ZrO_2 nanoparticles and ZrO_2–SiO_2 nanorods have been successfully used as matrices for cyclodextrins in atmospheric pressure and vacuum MALDI. The LOD for cyclodextrins was found to be 7.5–20 fmol and the matrices were used to analyze cyclodextrins in urine samples (Kailasa & Wu, 2010). Manganese dioxide nanoparticles have been used to ionize ginsenosides with the advantage that the spectra lacked matrix ions in the low mass region allowing low-mass post-source decay (PSD) ions to be clearly visible. The technique was named nanoparticle-assisted laser desorption/ionization (nano-PALDI) (Sahashi, Osaka, & Taira, 2010).

C. Other Matrices for Small Carbohydrates

Single-crystalline EuF_3 hexagonal microdisks with hollow interiors have been prepared as background free matrices. The long-lived excited state of europium ions is capable of transferring energy to the molecules allowing the microdisks to act as matrices. They were successfully used for analysis of small peptides, amino acids and hydroxypropyl β-cyclodextrin (**9**) (Chen et al., 2009d). Another new matrix with low background is mesoporous silica, SBA-15, functionalized with quinoline (Li et al., 2009d). The material was obtained by using calcined SBA-15 and 8-hydroxy-quinoline (**10**). Compared with DHB and SBA-15 itself, the modified material demonstrated several advantages in the analysis of small molecules such as less background interference ions, high homogeneity, and better reproducibility. Detection limits in the region of 8 pmol were reported.

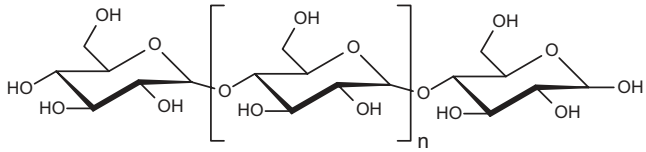


Hydroxypropyl β-cyclodextrin, **9**



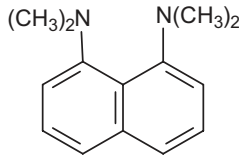
8-Hydroxyquinoline, **10**

In a more traditional approach for reducing low-mass matrix ions, Fujita et al. (2010) have used β-cyclodextrin (**4/6**) mixed with THAP or 2,4-DHAP. The latter compounds, in particular, formed inclusion complexes with the cyclodextrin as demonstrated by the lack of a similar effect when the corresponding linear carbohydrate, maltoheptaose (**11**) was used as a co-matrix.



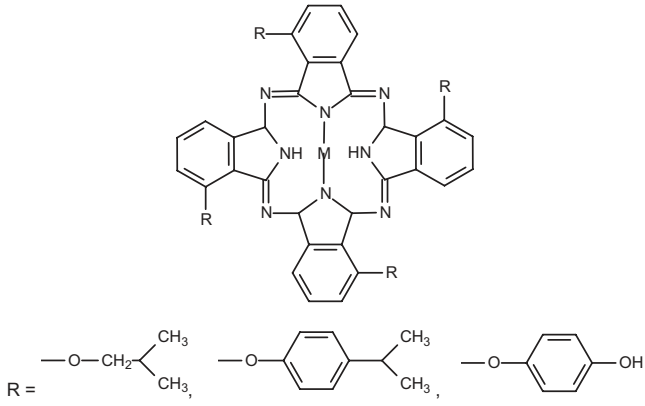
Maltoheptaose (n = 5), **11**

A method for recording negative ion spectra that is suitable for small molecules in that it produces no matrix-related ions in the low mass region uses the proton sponge, 1,8-*bis*(dimethylamino)naphthalene (DMAN, **12**) as a solution in ethanol as the matrix. This compound has very high proton affinity and can take up protons from even weak acids to form deprotonated anions. Moreover, DMAN in solution has a strong UV absorption band in the region 330–350 nm, fully compliant with frequencies of nitrogen and neodymium-doped yttrium aluminium garnet (laser) (Nd:YAG) UV lasers. The matrix was found to be suitable for a range of small molecules including fatty acids, carbohydrates and prostaglandins (Shroff & Svato, 2009; Shroff & Svatos, 2009; Shroff et al., 2009). The authors proposed to name the technique as matrix-assisted ionization/laser desorption, abbreviated as MAILD, MS (Shroff et al., 2009).



1,8-*Bis*(dimethylamino)naphthalene, **12**

Zhang et al. (2010i) have reported a new method for the analysis of small molecules by using matrices such as metal-phthalocyanines (MPc, **13**) which form matrix-analyte adducts and shift the molecular ions into a high and interference-free mass range. The mass of the target analyte was calculated by subtracting the mass of MPc from the mass of the MPc-analyte adduct. The MPcs themselves were also detectable and could serve as internal standards. Various MPcs with aromatic or aliphatic groups and different metal centers were explored. Aluminum-phthalocyanines (AlPcs), gallium-phthalocyanines (GaPcs), and indium-phthalocyanines (InPcs) were found to be efficient matrices for a large number of compound types and formed MPc-analyte adducts in either the positive or negative ion mode. The detection limits varied from 17 to 75 fmol, depending on analyte.



Metal-phthalocyanines, **13**

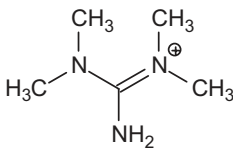
Graphene has also been reported to be a good matrix for low MW compounds with essentially no ions from the matrix (Dong et al., 2010). Colloidal graphite has also been used for atmospheric pressure MALDI and has been shown capable of producing both $[M+H]^+$ and $[M-H]^-$ from many types of small molecules, including glycosylated flavonoids (Perdian, Schieffer, & Houk, 2010).

D. Liquid Matrices

Two reviews on ionic liquids, including their use as MALDI matrices have been published (Soukup-Hein, Warnke, & Armstrong, 2009; Sun & Armstrong, 2010)

In an extensive study to find new liquid matrices 114 matrices were tested and 105 new ionic liquids were prepared (Crank & Armstrong, 2009). Both the anionic and cationic moieties were varied systematically to find a matrix with the best physical properties, analyte signal intensity and widest mass detection range. The developed matrices showed a wide mass detection range (<1,000 Da to >270,000 Da) for proteins and peptides with greater *S*/*N* ratios than solid matrices and could effectively ionize proteins of large mass without disrupting noncovalent interactions between monomers. It was found that both the proton affinity and pK_a of the cation have a large effect on the ability of the matrices ionize the analyte. The matrices could be used to detect carbohydrates with fewer degradation products than solid matrices. *N*,*N*-diisopropylethylammonium α-cyano-4-hydroxycinnamate and *N*-isopropyl-*N*-methyl-*t*-butylammonium α-cyano-4-hydroxycinnamate were the best matrices for proteins and peptides, while *N*,*N*-diisopropylethylammonium α-cyano-4-hydroxycinnamate and *N*,*N*-diisopropylethylammonium ferulate were found to be the best matrices for carbohydrates.

Another novel ionic liquid matrix has been made from the 1,1,3,3-tetramethylguanidinium (**14**) salt of THAP and found to be well suited for the MALDI analysis of glycopeptides and glycans, particularly as it appeared to overcome the well-known ionization suppression of carbohydrates in the presence of peptides. For example, even glycopeptides containing short peptide backbones and large carbohydrate moieties gave high signal intensities when using this matrix even though they did not produce spectra directly from THAP. In a second experiment, glycans were released with PNGase F from total tryptic digests derived from glycoproteins and analyzed by MALDI-quadrupole ion trap (QIT)-time-of-flight (TOF). When using the liquid matrix, it was possible to detect the glycans with high intensities in the presence of the tryptic peptides, whereas, once again, glycan ionization was completely suppressed when measured with THAP alone. The extent of metastable decay of glycopeptides was also found to be reduced when using the liquid matrix (Ullmer & Rizzi, 2009).

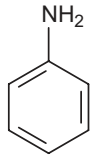


1,1,3,3-Tetramethylguanidine, **14**

Ionic liquid matrices have shown considerable advantages over conventional matrices for MALDI-MS analysis of polysulfated carbohydrates such as heparin and heparin sulfate. These compounds are not easily analyzed by UV-MALDI MS analysis because of the thermal lability of their *O*- and *N*-SO_3 moieties. Two new ionic liquid matrices based on the combination of 2-(4-hydroxyphenylazo)benzoic acid (HABA, **1/32**) with 1,1,3,3-tetramethylguanidine or spermine (**1/30**) have been successfully applied to the analysis of these compounds (Przybylski et al., 2010b). These matrices gave improved signal-to-noise ratios as well as a decrease of fragmentation and desulfation. Sulfated oligosaccharides were detected with higher sensitivity than with the usual crystalline matrices, and their intact sulfated ions $[MNa]^-$ were easily observed. MALDI-MS characterization of challenging analytes such as heparin octasaccharide carrying eight *O* and four *N*-sulfo groups, and heparin octadecasulfated dodecasaccharide was also successfully analyzed.

In a paper published in 2007, Gomenez et al. (2007) reported that DHB, with vacuum drying to improve target spot homogeneity, was a better matrix than sinapinic acid for obtaining reliable molecular mass values of intact glycoproteins because it prevented sugar fragmentation. In a follow-up to this work, the group have investigated the use of liquid matrices prepared from DHB and sinapinic acid with the aim of avoiding the vacuum drying step (Giménez et al., 2010). The best results were obtained with a variety of glycoproteins such as bovine α1-acid glycoprotein, bovine fetuin and human transferrin (TF) from matrices prepared by adding an equimolar amount of butylamine (64.1 μL) to 3,242 μL of a 200 mM solution of sinapinic acid or DHB in MeOH. The mixture was vortexed and sonicated for 1 min, evaporated to approximately 100 μL with air, and finally reconstituted with 100 μL of EtOH or MeCN, for DHB and sinapinic acid mixtures, respectively. Furthermore, it was noted that both matrices gave the same masses for the tested glycoproteins that agreed with literature values, suggesting that no fragmentation of the carbohydrate moieties had occurred.

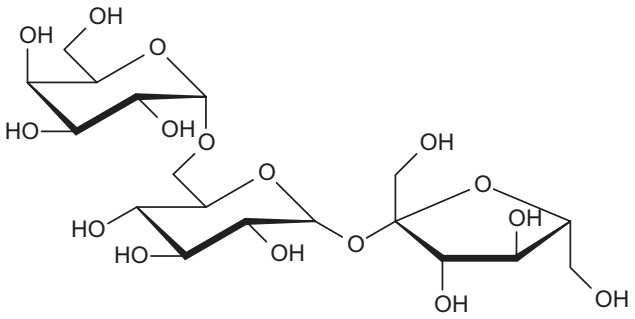
A matrix consisting of CHCA and aniline (**15**) has also proved to be successful for a number of different compounds, including raffinose (**16**) (Calvano, Carulli, & Palmisano, 2009). Although it was noted that this matrix gave a stronger signal than CHCA alone, the latter matrix is not very efficient in ionizing carbohydrates.



Aniline, **15**

E. Comparison of Matrices

A comparative investigation of several matrices for analysis of the small carbohydrates, glucose (Glc, **1/4**) and sucrose (**6**) has been performed by Yang et al. (2010c). Of the matrices studied, sodiated DHB, carbon nanotubes, an ionic liquid matrix of DHB-pyridine, a binary matrix of DHB-aminopyrazine (**6/7**),

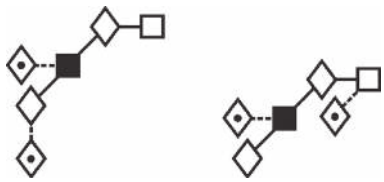


Raffinose, **16**

zinc oxide nanoparticles and AuNPs, the best sensitivity was provided by the carbon nanotubes. The detection limit was 3 pmol. Both carbon nanotubes and the ionic liquid matrix exhibited the highest reproducibility.

F. Sample Preparation

Tzeng, Zhu, and Chang (2009) have investigated doping various MALDI matrices with alkali metal hydroxides. It was found that for neutral underivatized oligosaccharides, the addition of 2% NaOH to DHB caused partial alkaline degradation by glycosidic cleavages upon laser desorption. The effect intensified when nonacidic compounds such as THAP or 5-amino-2-mercapto-1,3,4-thiadiazole (AMT, **4/7**) were used as the matrix. The degradation allowed identification of the reducing end residue of the analyte and facilitated its structural characterization by PSD TOF-MS. Use of matrices consisting of LiOH and THAP or AMT led to the production of singly as well as multiple lithiated ions. Multiple lithiation appeared to occur with carbohydrates containing free 3-OH groups. Up to 6 Li atoms were found to be incorporated for maltoheptaose, β-cyclodextrin, and dextran 1500. Such a "lithium tagging" technique makes it possible to differentiate positional isomers of milk-neutral oligosaccharides, lacto-*N*-difucohexaose I and II (LNDFH-I (**17**) and LNDFH-II, (**18**)), without the need of chemical derivatization or tandem MS analysis.



LNDFH-I, **17** LNDFH-II, **18**

■ = GlcNAc, ◇ = galactose, ◈ = fucose, □ = glucose

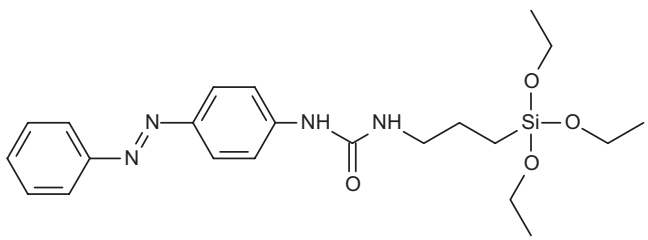
(for details, see (Harvey, et al., 2009c)

Choi and Lee (2009) have studied the ionization efficiencies of maltooligosaccharides (degree of polymerization, DP 1–7) with the cations Na^+, Li^+, and K^+ in salts containing TFA^-, Cl^-, and OH^- with DHB as the matrix. The signal strength rose with the number of glucose units with sodium consistently giving the most intense signals. The nature of the anion also affected the ionization with the TFA^- salts generally being the most effective.

A sample preparation method developed by Nishikaze and Amano (2009) has been compared with the conventional dried-droplet or ethanol (EtOH) recrystallization methods and reported to give superior results in terms of ion yield and signal-to-noise ratio. The method, named the "reverse thin layer method" consists of first, complete drying of the oligosaccharide solution on the MALDI target plate and then deposition of the matrix dissolved in a small amount of MeOH. Using this method, a relatively homogeneous matrix crystal was generated and higher yields of both positive and negative ions were obtained. The authors comment that the method could be applied to various other matrices including both solid and liquid matrices.

A method for direct archaebacterial glycolipid and lipid analysis by MALDI MS in intact membranes, without prior extraction/separation steps, has been developed by Angelini et al. (2010). The purple membrane isolated from the extremely halophilic archaeon *Halobacterium salinarum* was used as a model, lyophilized and ground with 9-aminoacridine (9-AA, **6/18**). The mixture was crushed in a mechanical die press to form a thin pellet, small pieces of which were attached directly to the MALDI target. In parallel, solution spectra of individual phospholipids and glycolipids, were analyzed by MALDI-TOF/MS using 9-AA as the matrix. Results show that 9-AA is a suitable matrix for the conventional MALDI-TOF/MS analysis of lipid extracts from archaeal microorganisms, as well as for fast and reliable direct dry lipid analysis of lyophilized membranes.

A new technique termed matrix-free material-enhanced laser desorption/ionization mass spectrometry (mf-MELDI-MS) has been described which employs a single compound prepared by immobilizing bradykinin on silica gel coupled to 4-(3-triethoxysilylpropylureido)azobenzene (**19**) for both the MALDI matrix and a stationary phase for thin-layer chromatography (TLC). The technique was applied to the analysis of carbohydrate reference standards such as glucose, sucrose, raffinose and plant extracts from *Quercus robur* (oak). Carbohydrates formed $[M+Na]^+$ and abundant $[M+K]^+$ ions. The MELDI material adsorbs the laser energy sufficiently for desorption and ionization and delivered excellent results in respect to signal-to-noise (*S/N*) ratio (*S/N* ratio: >9/1) and sensitivity with a LOD in the low ng/mL range. For preparation of the TLC plates, the modified silica gel was suspended in methanol, acetone, acetonitrile or acetonitrile/water (1:1) for 3 min. About 15–20 mL of the suspension was applied in narrow channels cut into a stainless steel target in the form of a thin layer and dried at room temperature. The sample was placed on this layer for subsequent TLC in *n*-BuOH/acetone/acetic acid/H_2O (35:35:10:20) as mobile phase (Qureshi et al., 2010).



4-(3-Triethoxysilylpropylureido)azobenzene, **19**

TABLE 2. Reviews and General Articles on MALDI Imaging

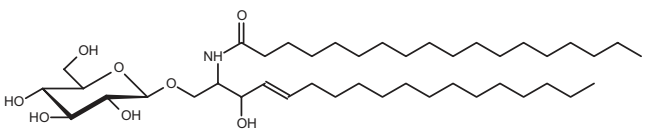
Subject	Contents	Citations	Reference
General review	Short article, mainly applications	50	(Murayama et al., 2009)
General review	Methods and applications to peptides and lipids (including glycolipids)	96	(Zaima et al., 2010)
General review	Short general review (Award lecture)	47	(Setou et al., 2010)
General review	From origins to state of the art	41	(Francese et al., 2009a)
Concise review of mass spectrometry imaging	General review including instrumentation and sample preparation	107	(Amstalden van Hove et al., 2010)
Mass spectrometric imaging for biomedical tissue analysis	Detailed review on most aspects of imaging	340	(Chughtai & Heeren, 2010)
Current imaging mass spectrometry for metabolite molecules	Applications to phospholipids, gangliosides and drugs	61	(Sugiura & Setou, 2009)
Imaging MS for visualization of drug and endogenous metabolite distribution	Short general review with section on drugs, lipids and glycosphingolipids	60	(Sugiura & Setou, 2010)
Choice of matrix for imaging	With table of matrices appropriate for different compounds	27	(Sugiura et al., 2010b)

V. MALDI IMAGING

MALDI imaging has seen many developments during the review period and several reviews and related articles have been published; details are in Table 2.

A. Methods for Producing High Resolution Images

A mass spectrometer with ion mobility separation capability (Waters Synapt) has been used by Snel and Fuller (2010) to produce high spatial resolution images of glucosylceramide (**20**) in the spleens of mouse models of Gaucher disease. The matrix (CHCA) was applied to the tissue sections with an airbrush. For data acquisition, the laser was continually fired at one position until no more ions were observed and then the sample was moved by 15 μm (laser diameter about 150 μm). Ions were generated from only the un-irradiated surface at each of these positions achieving an effective spacing of 15 μm. At this spacing, it was possible to visualize macrophages enriched in glucosylceramide which could be distinguished from other cell types in the spleen. Current MALDI mass spectrometric imaging (MSI) spatial resolution is typically limited by the diameter of the laser spot-size, which is usually between 50 and 100 μm, covering an area equivalent to tens of mammalian cells.



Glycosylceramide, **20**

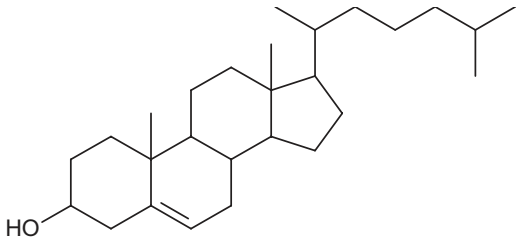
Perdian and Lee (2010) have addressed the problem of acquiring high resolution imaging with high resolution MS on an Orbitrap mass spectrometer. At a spatial resolution of 100 μm, the Orbitrap mass analyzer is able to image a $2{,}000 \times 2{,}000\ \mu m^2$ sample area in 7–14 min with one scan per step, depending on the resolution. If the spatial resolution is increased to 5 μm, the same size sample area will take more than 44–88 hr to complete the experiment, a time that is not practical in the normal laboratory. However, because the Orbitrap also has a linear ion trap (IT) analyzer, this was utilized, together with a two-motion plate movement to reduce the time while maintaining the resolution. Thus, for every pixel position on the target, the laser spot was moved in a spiral fashion such that both Orbitrap and MS/MS data were acquired. With a fast Nd:YAG laser the data acquisition time was decreased by 43–49% compared to that from orbitrap-only scans; however, 75% or more time could be saved for higher mass resolution and with a higher repetition rate laser. Using this approach, a high spatial resolution of 10 μm was maintained at IT imaging, while Orbitrap spectra were acquired at a lower spatial resolution, 20–40 μm, all with far less data acquisition time. Furthermore, various MS imaging methods were developed by interspersing MS/MS and MS fragmentation n times (MS^n) IT scans during Orbitrap scans to provide more analytical information. The method was applied to several flavonol glycosides from an *Arabidopsis* flower petal in which MS/MS, MS^n, IT, and Orbitrap images were all acquired in a single data acquisition. Spectra were acquired in negative mode and no matrix was required.

B. Matrix-Free Methods

For UV-absorbing compounds such as flavonoids and their glycosides, a matrix is not necessary for imaging as demonstrated by imaging at the single cell level of secondary metabolites in *Arabidopsis thaliana* and *Hypericum* species (Hölscher et al., 2009). The highest spatial resolution achieved, 10 μm, was much higher than that achieved by commonly used MALDI) imaging protocols.

A new matrix-free technique called nanostructure-initiator mass spectrometry (NIMS) has been developed for the analysis

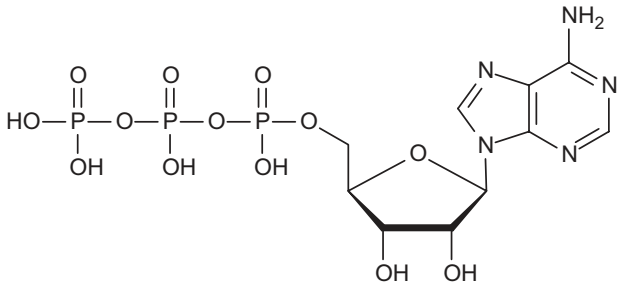
and tissue imaging of carbohydrates and steroids (Patti et al., 2010). Analysis was accomplished by spray depositing NaCl or $AgNO_3$ with a fused-silica PicoTip emitter onto a porous silicon surface to provide a uniform layer rich with cationization agents prior to desorption of the fluorinated polymer initiator. Upon laser irradiation, carbohydrates produced $[M+Na]^+$ ions whereas steroids formed $[M+Ag]^+$. For glucose, a plot of concentration against the $^{12}C/^{13}C_6$ ratio was linear with a correlation coefficient R^2 of 0.9975 over the range 1–200 mM. Carbohydrates and steroids could be detected down to the 800-amol and 100-fmol levels, respectively. The ability of the method to perform tissue imaging was demonstrated by imaging the distribution of sucrose in a *Gerbera jamesonii* flower stem and the distribution of cholesterol (**21**) in a mouse brain. The flower stem and brain sections were placed directly on the ion-coated NIMS surface without further preparation and analyzed directly. No deposition of a matrix onto the sample surface was needed.



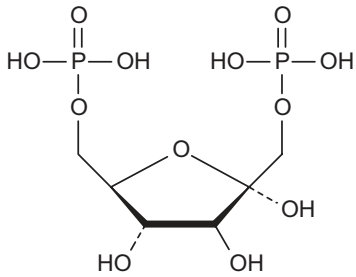
Cholesterol, **21**

A similar matrix-free method, termed nano-assisted laser desorption-ionization (NALDI) MS for tissue imaging has been demonstrated by Vidová et al. (2010). Commercially available nano-structured surfaces were used as substrates for imprinting tissue sections. The lithographic transfers were washed and the lipids were imaged by laser desorption mass spectrometry (LDMS). The NALDI imaging of lipid transfers was compared with standard MALDI imaging of matrix-coated (CHCA) tissue sections and the resulting images were found to be of the same quality with no spatial information being lost due to the imprinting process. NALDI imaging was reported to be faster due to the absence of the time-consuming matrix deposition step, and the NALDI mass spectra were less complex and easier to interpret than MALDI spectra. The method was applied to the analysis of phospholipids, GSLs and glycerophospholipids in mouse kidney slices. NALDI MS was able to identify the same lipid species as MALDI and was reported to provide better distinction between kidney and adrenal gland tissues based on the lipid analysis.

Miura et al. (2010a) have developed a MALDI imaging system that is claimed to be able to image from single cells in thin tissue sections. An indium tin oxide-coated glass slide marked with a 50 μm-wide mesh work to enabled matching of optical and MS images was used for mounting tissue sections. A suspension of HeLa cells in culture medium was mounted onto the slide and incubated for 6 hr at 37˚C. Cells were then washed with phosphate-buffered saline (PBS) and the appearance of single cells adhering to the glass was observed by optical imaging. The single cell-adhered glass slide was then mounted onto MALDI sample plate with a parallel experiment involving brain tissue slices and the matrix, 9-AA, was applied with an airbrush. Several metabolite peaks were detected at the position of the single cell. Adenosine triphosphate (ATP, **22**; *m*/*z* 505.99, identified by comparison with a standard sample) was identified with a good signal-to-noise ratio. Peaks were also obtained from other metabolites such as fructose-1,6-bisphosphate (**23**) and citrate. The report was claimed to be the first showing single cell metabolite analysis by MALDI-MS.



Adenosine triphosphate, **22**



Fructose-1,6-bisphosphate, **23**

C. Imaging of Gangliosides and Other Glycolipids

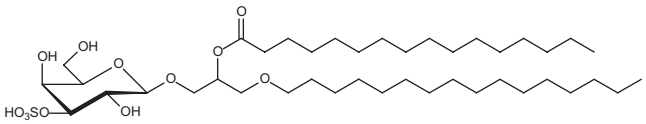
A major hurdle for imaging gangliosides in tissue using MS is that sialic acid residues can be dissociated in the ionization process. Chan et al. (2009a) have investigated the ionic liquid matrix CHCA/1-methylimidazol (**6/62**) (1:1 w/w) and have found that it produces excellent sensitivity for ganglioside detection without significant loss of sialic acid residues. The matrix was applied to the tissue samples with an airbrush; the method best adapted to handling a mixed matrix whose components have different volatilities. Image analyses of mouse brain tissue sections demonstrated that the *N*-fatty acyl chains of gangliosides were differentially distributed in mouse hippocampal regions. Gangliosides with *N*-C18 acyl chains were enriched in the CA1 region, while gangliosides with *N*-C20 acyl chain were enriched in dentate gyrus.

Colsch and Woods (2010) have developed a method for imaging sialylated GSLs in mouse brain. The total glycolipid profile was obtained by MALDI-TOF following solvent extraction and then individual species were mapped from frozen brain slices by MALDI using a linear TOF/TOF system in negative ion mode. The matrix, which consisted of saturated 2,6-dihydroxyacetophenone (DHAP, **1/49**) dissolved in 50% ethanol with the addition of ammonium sulfate (125 mM) and 0.05% of heptafluorobutyric acid (HFBA) was applied with a CHIP-1000 chemical inkjet printer with a piezoelectric head. Twenty-eight

nanoliters of matrix were deposited per spot with the distance between two spots of 240 μm. The ammonium sulfate in the matrix mixture limited the formation of salt adducts, while the addition of HFBA increased the stability of DHAP in the vacuum and reduced its rapid sublimation. Some sialic acid loss was noted, particularly with GD1 and GT1, which were detected as the ganglioside (β-D-Gal*p*-(1 → 3)-β-D-GalNAc[αNeu5Ac-(2 → 3)]-β-D-Gal*p*-(1 → 4)-β-D-Glc*p*(1 → 1)Cer) (GM1). The results showed differences in GSL localization in several brain regions depending on the sialic acids and the ceramide (Cer).

Imaging of lipids, including GSLs, has been reported by Landgraf et al. (2009) using a hybrid linear IT/Orbitrap mass spectrometer that allowed the acquisition of MS/MS spectra. A dramatic improvement in mass spectral resolution and a decrease in background were observed from lipids distributed within nerve tissue when compared with results obtained from fragmentation within the linear IT. The DHB matrix was applied to the dried tissue samples with an Epson inkjet printer and the MALDI ion source was operated at a pressure of about 75 mTorr. The technique was used to image lipids from rat spinal cord sections.

Goto-Inoue et al. (2009) have imaged the glycolipid, seminolipid (**24**) in mouse testis. This sulfated glycolipid comprises more than 90% of the glycolipid in mammalian testis and disruption of the gene catalyzing transfer of galactose (Gal) results in male infertility due to the arrest of spermatogenesis. Different molecular species are defined by fatty acid composition. Tissue imaging was performed from thaw-mounted tissue slices that had been sprayed with DHB with an airbrush. It was found that the major molecule (C16:0-alkyl-C16:0-acyl) was expressed throughout the tubules: some (C16:0-alkyl-C14:0-acyl and C14:0-alkyl-C16:0-acyl) were predominantly expressed in spermatocytes and the other (C17:0-alkyl-C16:0-acyl) was specifically expressed in spermatids and spermatozoa. This is the first report to show the cell-specific localization of each molecular species of seminolipid during testicular maturation. Experimental details for performing imaging of glycolipids using the airbrush application method for applying DHB, as used by this group, has been published separately (Goto-Inoue, Hayasaka, & Setou, 2010a).

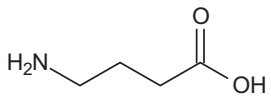


Seminolipid, **24**

The distribution and localization of GSLs present in mouse brain sections have also been investigated using nanoparticle-assisted laser desorption/ionization imaging MS. AuNPs modified with alkylamine were used as a new matrix to maximize the detection of GSLs. The mouse brain was frozen in liquid nitrogen, and serial sections were thaw-mounted onto indium-tin oxide (ITO)-coated glass slides. A thin layer of AuNPs or DHB matrix was applied to the surface with an airbrush. IMS analyses were performed by raster-scanning in the *x*-axis with a scan pitch of 200 μm in the *y*-axis. Sulfatides and gangliosides were detected in mouse brain sections with the new matrix whereas it was difficult to detect them using DHB (Goto-Inoue et al., 2010c). An oscillating capillary nebulizer (OCN) was also used by Chen et al. (2010g) for analysis of sphingolipids in tissue slices in Tay-Sachs/Sandhoff disease.

D. Imaging of Plant Tissues

In addition to the above-mentioned matrix-free methods, Jung et al. (2010) have reported imaging of cellulose in poplar (*Populus deltoids*) stem using more traditional techniques. Analysis of microcrystalline cellulose was performed first to determine the best matrix. DHB gave much stronger signals than matrices such as CHCA or sinapinic acid and was applied to poplar cellulose with an OCN. Ions at *m/z* 1,500, 2,472, and 3,120 (DP 9, 15, and 19) were monitored with a Voyager DE STR instrument and produced images that closely resembled the optical image. Taira et al. (2010a), on the other hand used an airbrush with CHCA to image ginsenosides in cross-sections of *Panax ginseng* root and used MS/MS to obtain detailed structural information. Ginsenosides were found to be located more in the cortex and periderm than in the medulla and that they were at greater concentration in the root tip than in the center of the root. Several carbohydrates including hexoses (Hex) and D-fructose 6-phosphate have been imaged in eggplant (*Solanum melongena*, also known as aubergine) fruits from DHB although the paper was mainly concerned with imaging of γ-aminobutyric acid (GABA, **25**) (Goto-Inoue, Setou, & Zaima, 2010b).



γ-Aminobutyric acid (GABA), **25**

Li, Bohn, and Sweedler (2010h) have compared two MS imaging methods, MALDI and SIMS, for glycan detection in the stems of the perennial grass *Miscanthus* × *giganteus*. Several methods of sample preparation were investigated for MALDI. A thin (2 nm) gold coating provided high quality signals of oligosaccharide-related ions and DHB also showed high efficiency for ion production. On the other hand, CHCA produced only very weak spectra, consistent with its use as a stand-alone matrix for carbohydrates. Direct laser ablation of untreated sections gave high resolution images, although coating the sections with a nanometer thick layer of gold greatly enhanced the quality of the SIMS images.

VI. DERIVATIVES

Two reviews describing derivatization reactions have been published (Busch, 2010; Ruhaak et al., 2010b), the second (207 references) is more comprehensive and deals specifically with *N*-linked carbohydrates.

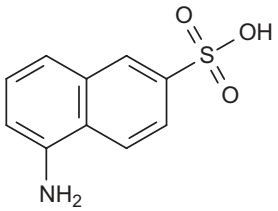
A. Reducing Terminal Derivatives

1. Reducing Terminal Derivatives Prepared by Reductive Amination

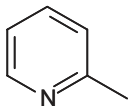
These derivatives are most often used for introducing fluorescent tags for chromatographic detection but also find use in MS.

2-Aminobenzamide (2-AB, **1/56**) and 2-aminopyridine (2-AP, **1/52**), favored by Japanese investigators, are the derivatives most frequently encountered; use of the latter derivatives has been reviewed by Hase (2010).

Several new derivatives (or labels) have been reported. Thus, 5-amino-2-naphthalenesulfonic acid (ANSA, **26**) has been used to derivatize *N*-glycans by reductive amination for capillary electrophoresis (CE), HPLC, and MALDI-TOF analysis (Briggs et al., 2009). The derivative was reported to give superior resolution in both CE and HPLC analysis to the well-used 8-aminopyrene-1,3,6-trisulphonic acid (APTS) derivatives and in MALDI-TOF analysis, the negative charge enabled both neutral and acidic glycans to be examined simultaneously. 3-Amino-9-ethylcarbazole (**6/19**) (Mou et al., 2009), another new derivatizing agent, has been reported to increase sensitivity of MS detection. 2-Picoline-borane (**27**) has been proposed as an alternative to toxic sodium cyanoborohydride for the reductive amination reaction (Ruhaak et al., 2010a).

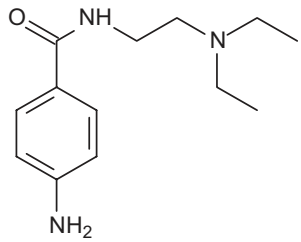


5-Amino-2-naphthalenesulfonic acid, **26**



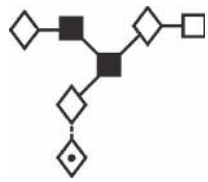
2-Picoline-borane, **27**

Pabst et al. (2009) have compared the preparation and performance of 15 different labels for *N*-glycan analysis. Several cleanup procedures were developed for cleaning these derivatives before analysis, of which hydrophilic interaction solid-phase extraction (SPE) appeared to be the most widely used. However, the cleanup was laborious and a better method was sought. Simple addition of acetone resulted in the formation of a precipitate, which turned out to be the labeled oligosaccharide. A single addition and removal of acetone reduced the amount of reagent to approximately 0.2% (measured with 2-AB). Two further extractions of the pellet with acetone reduced the excess of amine reagent by at least as much as clean-up with a cyano-SPE cartridge. In addition, reduction of the Schiff base of 2-AP-labeled glycans proceeded faster and/or required less reagent when the samples were pre-purified before the addition of reducing agent. Acetone extraction was successfully applied to many other labels such as 2-AB and 3-aminobenzoic acid (2-AA) (**1/57**). With respect to the performance of the individual labels, procainamide (**28**) emerged as more sensitive than 2-AA for normal-phase HPLC, but its chromatographic performance was not convincing. 2-AP gave the lowest retention on reversed-phase and graphitic carbon columns and, thus, appeared to be most suitable for glycan fractionation by multidimensional HPLC. Most glycan derivatives performed better than native carbohydrates in MALDI and ESI MS, but the sensitivity gain was small and hardly sufficient to compensate for sample loss during preparation.



Procainamide, **28**

Amano et al. (2009a) have labeled oligosaccharides with a pyrene derivative in order to acquire negative ion MALDI-QIT-TOFMS^n spectra. The oligosaccharides were reacted with pyrene butanoic acid hydrazine (**6/21**) and then reduced with $NaBH_4$ and cleaned with a small C_{18} column. The derivatives gave intense and stable molecular ions in both positive and negative ($[M-H]^-$ ions) modes and as little as 10 fmol of pyrene-labeled oligosaccharides, such as monofucosyllacto-*N*-hexaose (**29**) gave sufficient signals for analysis. Although some fucose loss by in- and post-source occurred in positive ion mode, this loss was significantly less in negative mode.

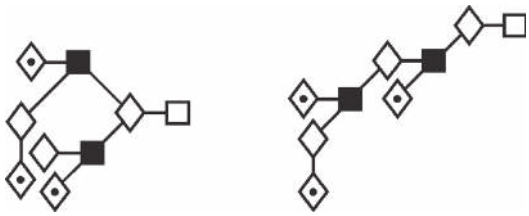


Monofucosyllacto-*N*-hexaose, **29**

A method, termed glycan reductive isotope labeling (GRIL) has been introduced for glycan quantitation. Free glycans or those released from glycoproteins, were derivatized by reductive amination with either [$^{12}C_6$]aniline or [$^{13}C_6$] aniline. These dual-labeled aniline-tagged glycans could be recovered by reversed-phase chromatography and could be quantified by UV absorbance or MS. One labeled variety was used as the reference standard against which the test glycan, labeled with the other isotope was measured. Unlike previously reported isotopically coded reagents for glycans, the derivatives did not contain deuterium, which can sometimes be chromatographically resolved. The technique allowed linear relative quantitation of glycans over a 10-fold concentration range and could accurately quantify sub-picomole levels of released glycans (Xia et al., 2009).

On-target derivatization with the matrix 3-aminoquinoline (**1/24**) has yielded Schiff bases which could be measured directly in positive and negative ion mode from one single spot. The optimal conditions were 20 mg/mL of 3-AQ in a MeCN-water mixture (1:2 v/v) with 0.07% of an inorganic acid to give a pH of 5. In negative ion mode, spectra from chloride adducts of the derivatives were acquired from 1 fmol of oligosaccharide. Furthermore, PSD fragmentation in positive and negative ion mode was enhanced, providing information on oligosaccharide sequence, linkage, and branching. The method was applied to

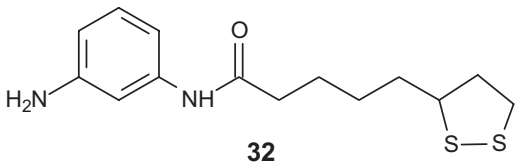
trifucosyllacto-*N*-hexaose (**30**) and trifucosyl-*para-lacto-N*-hexaose (**31**), two isomers occurring in human breast milk samples, which were easily identified and distinguished (Rohmer et al., 2010).



TFLNH, **30** TFpLNH, **31**

(Symbols as defined for structures 17 and 18. Anomericity not specified)

Reductive amination derivatization has also been exploited in other areas, combined with their use in MS. Binding of sugar chains to proteins, viruses and cells is conveniently monitored by the surface plasmon resonance (SPR). Key to this method is the use of linker compounds for immobilization of the sugar chains to the gold-coated SPR chip. Sato et al. (2009a) have developed a novel linker molecule, named "f-mono," which combines a linker with a fluorescent moiety to allow high sensitivity monitoring of the glycans. Since the molecule (**32**) contains a 2,5-diaminopyridyl group and a thioctic acid group, conjugation with sugar chains can be achieved by the reductive amination reaction. The mass spectra of thee compounds contained a peak 2 Da higher than the molecular ion due to the reduction of the thioctic acid moiety providing a convenient method for identifying the glycans even using unfractionated crude samples. Immobilization of the derivatives onto gold-coated chips, and their subsequent SPR analyses were successively accomplished.

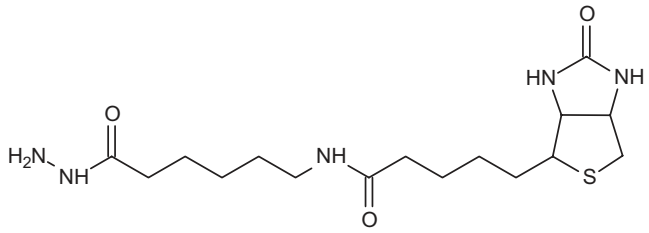


32

2. *Hydrazones*

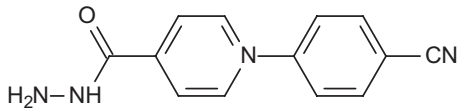
Use of hydrazone formation removes the need for a reductive step to stabilize the derivative as required by Schiff base formation from primary amines. Experimental details for synthesis of the phenylhydrazone derivatives discussed in earlier reviews (Lattova & Perreault, 2003a,b; Lattova, Perreault, & Krokhin, 2004) have recently been reported in an edition of *Methods in Molecular Biology* devoted to glycomics (Lattová & Perreault, 2009).

Small oligosaccharides and *N*-glycans from chicken ovalbumin have been converted into their biotin derivatives by incubating them with biotinamidocaproyl hydrazide (BACH, **33**) (Kapková, 2009). The derivatives imparted improved mass spectral sensitivity over that of the free glycans and, because the labeling reagent contained a biotin handle, it allowed the interaction between lectins and biotin-derivatized oligosaccharides to be investigated. Fragmentation of the *N*-linked glycans was dominated by Y and B/Y-type glycosidic ions.



BACH,**33**

Han et al. (2010a) have used a new substituted hydrazine, 1-(4-cyanophenyl)-4-piperidinecarbohydrazide (**34**) and produced a derivative that increased detection sensitivity by about 10-fold over that from the underivatized glycan. The observation of $[M+Na]^+$ ions rather than the expected $[M+H]^+$ species suggested that the sensitivity increase was the result of increased hydrophobicity. MALDI analysis employed DHB and super-DHB; recrystallization of the super-DHB sample with acetonitrile substantially improved the signal-to-noise ratio and reproducibility.

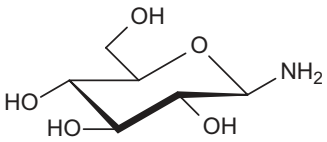


1-(4-Cyanophenyl)-4- piperidinecarbohydrazide, **34**

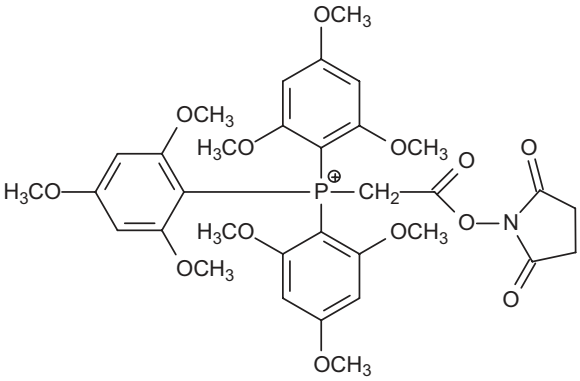
Girard's T reagent (**1/55**), with its constitutive cationic charge, has been used in quantitative measurements, as described below and for measuring α-galactose-containing *N*-glycans in porcine pig corneal endothelial cells and keratocytes (Kim et al., 2009c). Because of the in-built charge, signal strengths from glycans of different structures were thought to be equal. This is not necessarily the case for formation of $[M+Na]^+$ ions.

3. *Reducing-Terminal Derivatives Prepared by Other Methods*

Rather than reacting the reducing-terminal aldehydes of carbohydrates with amines or hydrazines, the reverse reaction can be used if the glycan is first converted into its glycosylamine (**35**). In fact, this type of reaction can be used directly on PNGase F-released *N*-glycans because these are released in this form. Chemical formation of glycosylamines generally utilizes the Kochetkov reaction in which the glycan is treated with an excess of ammonium carbonate. Unfortunately, this reaction is slow and can take up to five days for completion. To overcome this problem, Liu, Salas-Solano, and Gennaro (2009h) have used microwave assistance to speed the reaction up to as little as 90 min. Following amidation the glycans were reacted with *tris*-(2,4,6-trimethoxyphenyl)phosphonium acetic acid *N*-hydroxysuccinimide ester (**36**) to introduce a permanent charge on the glycan and the investigators were able to detect derivatized maltoheptaose at 2 fmol/μL by MALDI-TOF MS using DHB and CHCA matrices. Glycans from RNaseB, chicken ovalbumin and asialofetuin were also detected at high sensitivity. A potential problem arises from possible cleavage of the reducing-terminal *N*-acetylglucosamine (GlcNAc) residue as such a reaction has recently been reported as a by-product of the Kochetkov reaction when, for example, ammonium bicarbonate at 37°C was used (Murase & Kajihara, 2010).

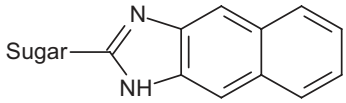


β-Glucosylamine, **35**

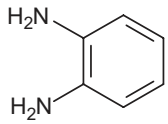


Tris-(2,4,6-trimethoxyphenyl)phosphonium acetic acid *N*-hydroxysuccinimide ester, **36**

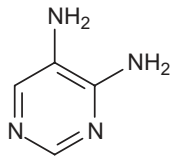
Several carbohydrates, including maltoheptose, blood type B antigen, pullulan and the glucan of *Ganoderma lucidum* have been converted into their naphthimidazole (NAIM) derivatives (**37**) in high yields by the iodine-promoted oxidative condensation (Scheme 1; Lin et al., 2010b). The reaction took about 6 hr to go to completion giving derivatized carbohydrates that gave enhanced MALDI signals ($[M+H]^+$ ions) compared with those from the free carbohydrates or their 2-AB derivatives with DHB or THAP as matrices. Less than 1 pmol of carbohydrate could be detected. Furthermore, the derivatives could easily be hydrolyzed to the parent glycans. A further series of such derivatives has been synthesized by condensation with diamines such as substituted benzene-1,2-diamine (**38**) in order to increase hydrophobicity and detection sensitivity (Lin et al., 2010c). Using maltotriose (**11**, $n = 1$), derivatives with pyrimidine-4,5-diamine (**39**), pyridine-3,4-diamine (**40**) and 1,2,5-oxadiazole-3,4-diamine (**41**) gave the strongest signals.



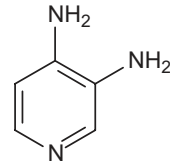
Naphthimidazole (NAIM) derivatives, **37**



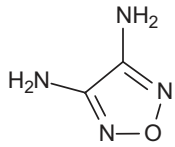
Benzene-1,2-diamine, **38**



Pyrimidine-4,5-diamine, **39**



Pyridine-3,4-diamine, **40**



1,2,5-Oxadiazole-3,4-diamine, **41**

B. Derivatives of Other Sites

1. Hydroxyl Groups—Permethylation

Permethylation has long been used in carbohydrate analysis, most frequently for linkage determination by gas chromatography/mass spectrometry (GC/MS) following hydrolysis and acetylation (permethylated alditols acetates). However, there appears to be an increasing trend to employ the reaction for MALDI analysis. The advantage of permethylation is that it increases sensitivity and several investigators employing its use appear to detect larger glycans, particularly *N*-glycans, than by the use of underivatized glycans. However, sample clean-up of the highly basic reaction mixtures can be a problem with, in some cases, losses offsetting any gain in sensitivity. Introduction of solid-phase permethylation has improved the situation. Experimental details of the solid phase permethylation method (methyl iodide on sodium hydroxide beads) (Kang, Mechref, & Novotny, 2008; Kang et al., 2005) that is capable of permethylating very small amounts of carbohydrate have been published in *Methods in Molecular Biology* (Mechref, Kang, & Novotny, 2009a). On the negative side, it has been reported that permethylation can lead to loss of *O*-linked acetyl groups from certain sialic acids (Liu & Afonso, 2010).

An extension of the solid-phase method to allow sulfated glycans to be analyzed by MALDI-TOF MS has been developed (Lei, Mechref, & Novotny, 2009). Sulfated glycan samples were permethylated followed by methanolytic cleavage of the sulfate groups. The desulfated, permethylated glycans were then subjected to another permethylation step using deuteromethyl iodide to label the hydroxyl groups that were exposed by removal of the sulfates. The number of attached sulfate groups could be calculated from the mass-shift caused by the presence of the deuterium label and the position of the sulfate substitution could be determined by collision-induced dissociation (decomposition) (CID). The method was validated with linear standard glycans and used to identify sulfated *N*-glycans released from bovine thyroid-stimulating hormone (bTSH).

Yu et al. (2009c) have shown that it is possible to permethylate sulfated glycans with methyl iodide and sodium hydroxide (Ciucanu and Kerek method) (Ciucanu & Kerek, 1984), without loss of the sulfated glycans. The trick is to avoid the normal chloroform/water partition stage, which results in much of the sulfated material (unmethylated) partitioning into the aqueous phase. Instead, clean-up employed C18 reversed-phase SPE cartridges and microtips self-packed with NH_2-

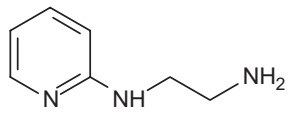
beads. The methylation reaction was capable of methylating phosphates but not sulfates, allowing them to be readily identified.

2. *Derivative Formation From Sialic Acids*

Formation of methyl esters by reaction of the sodium salt with methyl iodide has frequently been used to stabilize sialic acids to MALDI analysis by eliminating the labile proton on the acid group. An alternative procedure for methyl ester formation that provides information on the sialic acid linkage directly from the MALDI spectrum has been published by Wheeler, Domann, and Harvey (2009) (Fig. 2). The sugars were desalted, dried, dissolved in methanol and treated with 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-ethylmorpholinium chloride (DMT-MM, **5/12**). After removal of the solvent, the products were transferred directly to the MALDI target and examined from DHB. However, for the analysis of small amounts of *N*-glycans derived from biological sources, the method benefited from an additional clean-up stage involving the use of a Nafion 117 membrane. Unlike the reaction with methyl iodide with the sodium salt that produced a single peak from each sialylated glycan, irrespective of the linkage, the reaction with DMT-MM produced different derivatives from $\alpha2 \rightarrow 3$- and $\alpha2 \rightarrow 6$-linked sialic acids. The $\alpha2 \rightarrow 6$-linked sialic acids produced only methyl esters whereas $\alpha2 \rightarrow 3$-linked sialic acids were converted into their lactones providing a 32 Da difference in mass, thus enabling the linkage to be determined directly from the MALDI-TOF spectrum (Fig. 2). Negative ion CID mass spectra of these neutralized glycans provided information, in many cases, on the antenna of *N*-linked glycans to which the variously linked sialic acids were attached. In an application of the method to the glycoprotein carcinoembryonic antigen-related cell adhesion molecule 1 (CEACAM1), it was shown that both α-2 $\rightarrow$ 3- and α-2 $\rightarrow$ 6-linked sialic acids were present (Harvey, Baruah, & Scanlan, 2009a).

4-(4,6-Dimethoxy-1,2,3-triazil-2-yl)-4-methylmorpholinium chloride in the presence of ammonium chloride, converts sialylated glycans into amides with the same linkage-specific reactivity difference. Thus, the $\alpha2 \rightarrow 3$-linked sialylated glycans yield lactones, as above, whereas the $\alpha2 \rightarrow 6$-linked compounds form amides. Alley and Novotny (2010) have used this reaction to examine blood serum glycoproteins but their technique differed from the above methyl ester formation in that the glycans were permethylated after reaction with DMT-MM. This reaction formed the methyl ester from the $\alpha2 \rightarrow 3$-linked compounds as the result of the opening of the lactone ring, whereas the amide that was derived from the $\alpha2 \rightarrow 6$-linked compounds was converted into the corresponding dimethylamide with a 13 Da increase in mass over that of the methyl ester.

4-(4,6-Dimethoxy-1,2,3-triazil-2-yl)-4-methylmorpholinium chloride can also be used to form substituted amides directly and has been used by Endo et al. (2009) to link the fluorescent derivative 2-(2-pyridylamino)ethylamine (PAEA, **42**) to the carboxy group of sialic acids in sialo-oligosaccharides and gangliosides. The derivative gave good HPLC and TLC sensitivity and possessed the following advantages for MALDI analysis: suppression of preferential cleavage of Neu5Ac; enhancement of molecular-related ion intensities; simplification of MS spectra; and finally, since PAEA-amidation did not cleave the linkage between sugar and aglycon, allowed MALDI-TOF-MS and MS/MS analyses to reveal the complete structure of the molecule.



2-(2-Pyridylamino)ethylamine (PAEA), **42**

4-(4,6-Dimethoxy-1,2,3-triazil-2-yl)-4-methylmorpholinium chloride has also been used to form amides from hexuronic acids (HexAs) in an investigation of the *N*-linked glycosylation

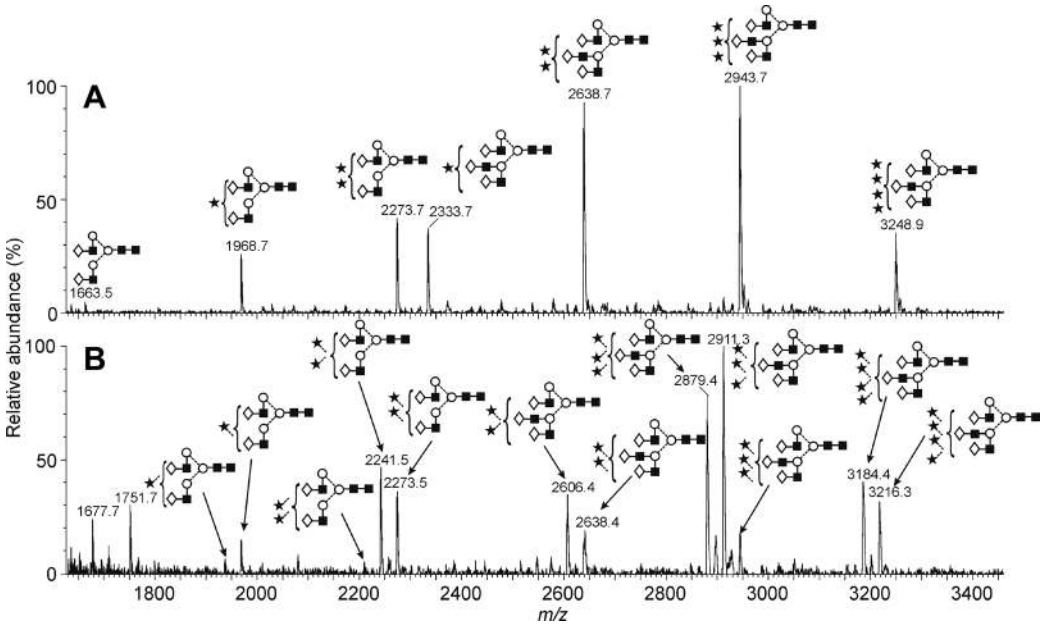
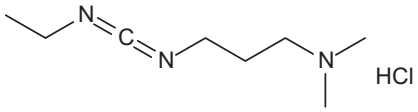


FIGURE 2. Positive ion MALDI-TOF spectrum of *N*-glycans released from bovine fetuin and derivatized with methanol in the presence of DMT-MM.

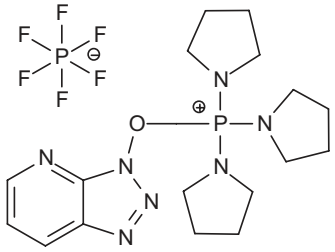
of structural subunit RvH2 of *Rapana venosa* hemocyanin (Dolashka et al., 2010). As well as containing the rather unsusal (for *N*-glycans) hexuronic acid, the glycans also contained naturally methylated hexoses and internal fucose residues.

Gil et al. (2010) have stabilized sialic acids by formation of amides with acetohydrazide under mild acidic conditions in the presence of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC, **43**). Glycoproteins were first reduced and alkylated and then the sialic acids were amidated. Glycans were released with PNGase F and a permanent charge was attached to the reducing terminus by further reaction with Girard's T reagent. Alternatively, derivatization with 2-AA was used and the products were examined both by HPLC and MALDI-TOF MS. The amidation reaction was performed on the glycoprotein because acetohydrazide would also have reacted with the aldehyde function of the released glycan, precluding derivatization with an amine more suited to the detection method used for monitoring the glycans. The method was applied to the analysis of *N*-glycans from transgenic pig-derived human factor IX.

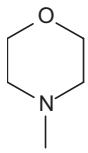


1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride, **43**

Another method for synthesis of methylamides has been reported by Liu et al. (2010i). Sialylated glycans were reacted with methylamine in the presence of (7-azabenzotriazol-1-yloxy)trispyrrolidinophosphonium hexafluorophosphate (PyAOP, **44**) and *N*-methylmorpholine (**45**) for 30 min at room temperature. After methylamidation, sialylated glycans were analyzed by MALDI-TOF and ESI MS without loss of the sialic acid moiety. Both $\alpha 2 \rightarrow 3$- and $\alpha 2 \rightarrow 6$-linked sialic acids were quantitatively converted to their methylamides. This method was validated with *N*-glycans released from the well-characterized glycoproteins, fetuin, human α1-acid glycoprotein, and bovine α1-acid glycoprotein and was used to study *N*-glycans from serum glycoproteins from human, mouse, and rat. Both Neu5Ac and *O*-acetylated analogues were stable under MALDI conditions.



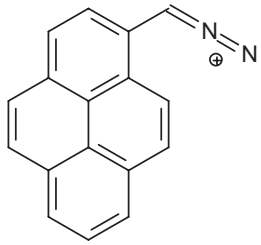
(7-Azabenzotriazol-1-yloxy)trispyrrolidinophosphonium hexafluorophosphate, **44**



N-Methylmorpholine, **45**

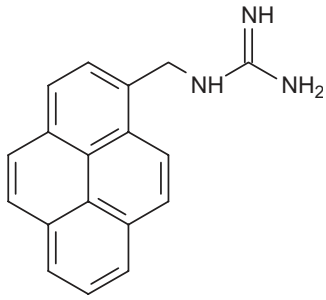
3. Other Derivative-Related Methods

Glycopeptides tend to produce weaker signals than nonglycosylated peptides and it is frequently difficult to observe their molecular ions in samples rich in unglycosylated peptides. Amano et al. (2010) have developed a highly sensitive on-plate pyrene derivatization method using 1-pyrenyldiazomethane (**46**) for acquisition of MALDI MS^n spectra of glycopeptides in amounts of less than 100 fmol. Unusually, the pyrene groups were easily released from glycopeptides during ionization when DHB was used as a matrix. Thus, most ions were observed in their underivatized form. At the same time, pyrene derivatization was found to reduce the ionization of peptides and to produce signals from the glycopeptides that were strong enough for acquisition of MS^n spectra that contained ions from both glycan and peptide. When the liquid matrix, 3AQ-CHCA, was used, the sialic acid linkages of the pyrene sialylated glycopeptides were found to be stable because of inefficient release of the pyrene group allowing MS^n spectra of the intact glycans to be obtained. The method was used to examine glycopeptides from 1 ng of prostate specific antigen.

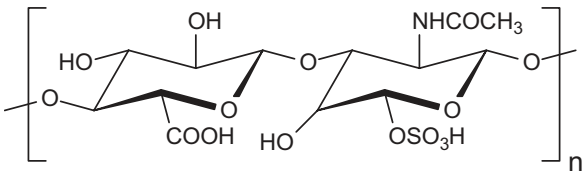


1-Pyrenyldiazomethane, **46**

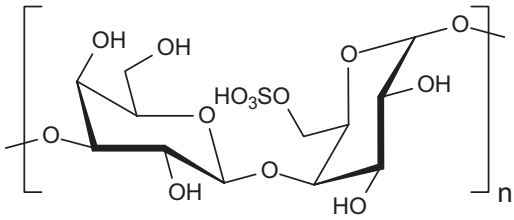
Ohara et al. (2009) have developed a method for analysis of sulfated carbohydrates by forming complexes with 1-(pyren-1-ylmethyl)guanidine (PMG, **47**) from a matrix consisting of this compound and *p*-nitroaniline (**3/3**). Two types of sulfated carbohydrate were examined, chondroitin sulfate (**48**) and carrageenan (**49**). The PMG complexed with the sulfate group and was eliminated under MALDI conditions such that the molecules produced a ladder of peaks separated by masses corresponding to losses of each complexed sulfate (mass difference 353 U). In positive ion mode, the molecular ions from the chondroitin sulfates contained one more PMG molecule than the number of sulfate groups. One PMG group was presumed to bind to a carboxylate group. In negative mode, one less PMG molecule was bound. Carrageenans showed a slightly different pattern in that the number of PMG molecules found in the positive ion spectra equaled the number of sulfates.



1-(Pyren-1-ylmethyl)guanidine, **47**

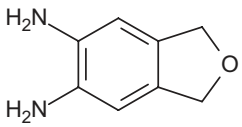


Chondroitin sulfate, **48**



γ-Carrageenan, **49**

Sialic acids are classically analyzed by HPLC after formation of fluorescent 1,2-diamino-4,5-methylenedioxybenzene (DMB, **50**) derivatives. These derivatives require an α-keto acid group in the sialic acid. Galuska et al. (2010b) have developed a method for specifically measuring nucleotide-activated sialic acids in the presence of unactivated acids by first reducing the keto group that is present only in the non-activated acids. Under the conditions of the derivatization reaction, the nucleotide group was removed leaving, in the case of the activated acids, only, an intact α-keto acid group that reacted with the DMB reagent. Subsequent analysis was by HPLC and MALDI-TOF.

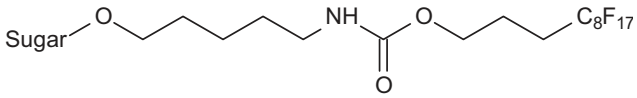


1,2-Diamino-4,5-methylenedioxybenzene, **50**

VII. GLYCAN ARRAYS

MALDI MS is used extensively in analyses with glycan arrays as summarized in recent reviews (see Table 3). Table 4 lists glycans that have been used in array construction.

Most of the above work has been with carbohydrate preparations prior to array construction. However, MALDI MS has also been used to interrogate arrays directly. As an example, a new type of glycan array covalently or non-covalently attached to aluminium oxide-coated glass slides has been developed for studies of enzymatic reactions and protein binding (Chang et al., 2010). The array was prepared by tagging glycans with a polyfluorinated hydrocarbon (**51**) tail and spotting them robotically onto the aluminium oxide-coated slide surface which contained a layer of polyfluorinated hydrocarbon terminated with phosphonate. After incubation and washing, the non-covalent array was characterized by MALDI-TOF at a low laser energy without addition of matrix. A cellotetraose (D-Glc-(β-(1 → 4)-D-Glc)$_2$-β-(1 → 4)-D-Glc) array was developed to study the activity and specificity of different cellulases and to differentiate the exo- and endoglucanase activities. Compared to the preparation of glycan arrays on glass slides and other surfaces, this method using phosphonic acid reacting with aluminium oxide-coated was said to be more direct, convenient and effective and represented a new platform for the high-throughput analysis of protein–glycan interactions.



Polyfluorinated hydrocarbon tag, **51**

In another application, a ligand affinity capture (LAC) method for detection of biotinylated biomolecules has been developed by Jørgensen, Juul-Madsen, and Stagsted (2009). Metal-coated glass slides were treated with amino-silane and derivatized with biotin followed by avidin. Biotinylated biomolecules could then be captured and detected in the low femtomole to low picomole range by MALDI-TOF MS using CHCA in a dried droplet method. The technique was used to detect biotinylated lipopolysaccharide (LPS) and its binding to the antagonist polymyxin B.

The α-mannose-specific lectin Concanavalin A (Con A) has been bound to polydopamine-modified gold, indium, and iridium surfaces and its activity was demonstrated with RNase B using SPR spectroscopy. Surface-MALDI-TOF MS experiments revealed that the affinity of the immobilized Con A depended on the oligosaccharide structure and composition. Thus Con A was found to bind certain Man_7- (**4/20**), Man_8- (**5/20**), and Man_9-$GlcNAc_2$ RNase B glycoforms more strongly than Man_5- and Man_6-$GlcNAc_2$ glycoforms (Morris, Peterson, & Tarlov, 2009).

VIII. QUANTIFICATION

Concern has frequently been expressed about the ability of MALDI-TOF MS to provide quantitative information. Fortunately, this concern appears to be unjustified as two recent studies have shown. Thus, a systematic study of widely different glycopeptides was performed by Thaysen-Andersen, Mysling, and Højrup (2009) to determine the relationship between the relative abundances of the individual glycoforms and the MALDI-TOF MS signal strength. Glycopeptides derived from glycoproteins containing neutral glycans (RNaseB, IgG, and ovalbumin) were profiled and yielded excellent and reproducible quantitation (correlation coefficient $r = 0.9958$, $n = 5$) when evaluated against a normal-phase HPLC 2-AB glycan profile. Similarly, precise quantitation was observed for various forms of *N*-glycans (free, permethylated, and fluorescence-labeled) using MS. In addition, three different sialo-glycopeptides from fetuin were site-specifically profiled, and good correlation between peak intensities and relative abundances was found with only a minor loss of sialic acids ($r = 0.9664$, $n = 5$). For glycopeptide purification, a range of hydrophilic and graphite materials packed in microcolumn format was evaluated and proved capable of desalting without loss of quantitative information. Thus, MALDI-TOF MS signal strength of glycopeptides has been found to accurately reflect the relative quantities of glycoforms, enabling rapid and sensitive site-specific glycoprofiling of *N*-glycan populations.

TABLE 3. Reviews on Glycan Arrays

Subject	Contents	Citations	Reference
Carbohydrate structure and array construction	Glycan overview. Biosensors and microarrays based on carbohydrate interactions	~260	(Chevolot et al., 2010)
Lectin and carbohydrate microarrays	New high-throughput methods for glycoprotein, carbohydrate-binding protein and carbohydrate-active enzyme analysis	80	(Fais et al., 2009)
Lectin microarrays for glycoprotein analysis	Short review of fabrication and detection systems	18	(Hu & Wong, 2009)
Techniques for glycomics with emphasis on arrays	General review with emphasis on arrays	170	(Krishnamoorthy & Mahal, 2009)
General review	Review of recent advances in glycan array technology	138	(Liang & Wu, 2009)
Glyconanoparticles	To study carbohydrate-based interactions	-	(Marradi et al., 2010)
Glycoprotein analysis using protein microarrays and mass spectrometry	Carbohydrate, glycoprotein, lectin and antibody microarrays	75	(Patwa et al., 2010)
Recent developments in fabrication and detection	Short general article on carbohydrate arrays	53	(Song & Pohl, 2009)
Enzymatic glycosylations on arrays	Review of on-chip glycosylations	38	(Voglmeir et al., 2010)
Perspective on glycan arrays	Short general overview	87	(Wu et al., 2009a)
Engineered nanoparticle surfaces for improved mass spectrometric analysis	Short minireview. Use of surface-engineered nanoparticles for analysis of several compound types	49	(Zhu et al., 2009b)

The second study relates to the concern that has often been expressed over possible losses of fucose residues when glycans are ionized by MALDI. Tajiri, Kadoya, and Wada (2009b) have recently assessed possible fucose loss and found it to be insignificant. Fucose (Fuc) is known, however, to migrate within $[M+H]^+$ ions particularly when these are derivatized by reductive amination. Experiments on fucose loss were conducted with fucosylated glycopeptides from TF and haptoglobin. Studies with increasing collision energy on the $[M+H]^+$ ions showed that the major fragmentation was cleavage at GlcNAc residues. Biantennary glycans containing α1,3/4-antenna fucose or α1,6-core fucose showed different fragmentation behaviors in experiments. Stability was dependent on peptide backbone sequences. Cleavage of the GlcNAcβ1 → 2Man linkage occurred at a slightly lower activation energy than for the core fucosylated (CF) species, while the linkage of α1,6-core fucose was more stable than that of antenna α1,3/4 fucose. However, these fragmentations only occurred at relatively high collision energy. Consequently, the authors concluded that quantitation of fucosylated glycans by MS of glycopeptides, without collisional activation, was justified. The fucosylation levels calculated from the signal intensities in nanospray ionization and UV MALDI mass spectra were essentially the same. The mass spectrometric profiling of glycopeptides from TF from patients with congenital disorders of glycosylation (CDG-Ia and CDG-IIc) demonstrated that the elevation or reduction of fucosylation in pathological conditions can be reliably determined by MS of glycopeptides.

In spite of these reassurancies, it is possible that for mixtures of compounds, complex suppression effects may degrade quantitative results. Consequently some investigators prefer LC/MS methods because the LC step removes, or minimizes, the effect that other compounds in a mixture have on the ionization of the target compounds.

Instability of sialylated glycans under MALDI conditions complicates quantification and errors can possibly also be introduced by unequal ionization of glycans in mixtures. To overcome these problems with *N*-glycans from a therapeutic glycoprotein from a Chinese hamster ovary (CHO) cell line, Jang et al. (2009a) first formed methyl esters of the sialic acids to stabilize them and then converted the glycans to their Girard's T derivatives. These derivatives have a constitutive positive charge, thus overcoming the problem of unequal ionization. Percentages of sialylated glycans were measured at 22.5 and 5.2% in two cell lines. The results were comparable to those obtained by NP–HPLC combined with fluorescence detection using 2-AB or 2-AP derivatization. Girard's T derivatives have also been used by Kim et al. (2009a) to quantify glycans released from GSLs originating from miniature pig endothelia and islet cells.

A method using a deoxyribonucleic acid (DNA) sequencer has been described for the quantitative analysis of plant *N*-glycans released with PNGase A or F and derivatized with APTS (**1/59**). MALDI-TOF analysis was used to confirm structures with the aid of exoglycosidase digestions (Lee et al., 2009i).

A method for the quantification of fructo-oligosaccharides using MALDI TOF MS with DHB as the matrix, has been developed with the fructan, raftilose, a partially hydrolyzed inulin with a degree of polymeration 2–7 as the test compound

TABLE 4. Glycans Used to Construct Glycoarrays

Carbohydrate	Methods[1]	Synthetic methods and/or comments	Reference
2-Amino-*N*-(2-aminoethyl)-benzamide (AEAB) fluorescent derivatives	TOF/TOF	Synthesis of fluorescent derivatives of glycans, construction of microarray and use for detecting galectin ligands	(Song et al., 2009d)
Bacillus anthracis tetrasaccharide with thiol linker	MALDI	For attachment to a maleimide functionalized Microarray to study of carbohydrate-antibody interactions	(Oberli et al., 2010)
Glycodendrimers with N_3 group terminating in α-Man, β-GlcNAc or β-Gal	TOF	Immobilized on an acetylenyl-terminated gold substrate *via* click chemistry	(Fukuda et al., 2009)
High-mannose glycans - Oxime linked	TOF	Used to probe binding to malectin	(Palma et al., 2010)
MUC1 Glycopeptides	TOF	Synthesis on an amine-reactive hydrogel-coated microarray glass surface. To detect autoantibodies in breast cancer	(Blixt et al., 2010) Correction: (Blixt et al., 2011)
N-Glycan-Asn-fmoc conjugates from chicken ovalbumin, bovine fetuin, and horseradish peroxidase (HRP)	TOF/TOF	Printed onto commercially available *N*-hydroxysuccinimide (NHS) -activated glass slides after deprotection. Glycans interrogated using plant lectins and antibodies in sera from mice infected with *Schistosoma mansoni*	(Song et al., 2009e)
N-glycan clusters	TOF (DHB)	Biantennary and high-mannose *N*-glycans linked to non-reducing terminus of $Man_3GlcNAc_2$ core, plus biotin	(Huang et al., 2009a)
N- and *O*-glycans, AEAB derivatives	TOF/TOF	Construction of arrays in which the cyclic form of the reducing terminal GlcNAc is retained	(Song et al., 2009c)
Glycoproteins	TOF	Enzymatic remodelling of *N*- and *O*-glycans for lectin binding studies	(Iskratsch et al., 2009)
Oligosaccharides from plants	TOF (DHB)	For construction of microarray to screen for plant transglycosidases activity	(Kosík et al., 2010)
Phosphorylated high-mannose glycans, AEAB derivatives	R-TOF	High-mannose glycans from ribonuclease. Incubation with recombinant GlcNAc phosphotransferase. For glycan microarrays	(Song et al., 2009f)
Thiol-terminated nonamannoside	TOF	Coupling of a thiol-terminated mannoside to maleimide-functionalized glass surfaces derived from γ -aminopropyl silane slides	(Dietrich et al., 2010)
Various oligosaccharides derivatized with 4-(2-aminoethyl)aniline by reductive amination	TOF (DHB)	Reagent has amine groups at both ends allowing the modified carbohydrates to be covalently attached to an amino-reactive NHS-activated glass surface by formation of stable amide bonds	(Seo et al., 2010)

(Onofrejová, Farková, & Preisler, 2009). Nystose (**2/11**), which is chemically identical to the raftilose tetramer, was used as the internal standard. Two mathematical approaches, conventional calculations and artificial neural networks (ANN), were compared for data processing. The conventional method relied on the assumption that a constant oligomer dispersion profile will change after the addition of the internal standard. On the other hand, ANN was found to compensate for a non-linear MALDI response and variations in the oligomer dispersion profile with raftilose concentration. As a result, the application of ANN led to lower quantification errors and excellent day-to-day repeatability compared to the conventional data analysis. This reproducibility was satisfactory for MS quantification of raftilose in the range of 10–750 pg with errors below 7%. The method was applied to measurements of the content of raftilose in dietary cream and it was stressed that no special optimization of the MALDI process was carried out.

MALDI-TOF MS with DHB, THAP or *p*-nitroaniline (**3/3**) has been used to determine the concentrations of the unsaturated disaccharide from chondroitin sulfate (**48**) obtained by enzymatic digestion of native chondroitin sulfate with chondroitin ABC lyase. The signal-to-noise (*S/N*) ratio in the spectrum was used as a quantitative measure: amounts of chondroitin sulfate (measured as the disaccharide) down to at least 500 fmol could be detected and there was a direct correlation between the S/N ratio and the amount of chondroitin sulfate between about 2 and 200 pmol although the curve was sigmoidal. The influence of different parameters such as the matrix, the applied laser intensity and different methods of data analysis were also tested. Advantages and drawbacks of this approach are critically

discussed in the paper. Finally, the method was validated by the determination of the chondroitin sulfate content in samples of known concentration as well as in enzymatically digested bovine nasal cartilage and compared with two further established methods of chondroitin sulfate determination (the carbazole and alcian blue methods) (Nimptsch et al., 2009).

IX. FRAGMENTATION

Positive ion fragmentation of carbohydrates is fairly well understood with two types of cleavage, glycosidic cleavage that occurs between the sugar rings and involve hydrogen migration and cross-ring cleavages that involve the rupture of two of the bonds forming the rings. Glycosidic cleavages revealing sequence information predominate in positive ion spectra whereas negative ion spectra frequently contain very abundant cross-ring product ions that provide information on linkage. The nomenclature introduced by Domon and Costello (1988) is universally used to describe the ions.

The stabilities of glycosyl bond linkages in various carbohydrates have been investigated by computational calculations to find general rules of fragmentation of sodiated oligosaccharides (Suzuki et al., 2009a). The calculations revealed that α-glucose, α-galactose, β-mannose, α-fucose, β-GlcNAc and β-GalNAc linkages were cleaved more easily than β-glucose, β-galactose, and α-mannose linkages because the transition states of the former were stabilized by the anomeric effect. The 1–6 linkage was more stable than the others whereas the sialyl bond was the most labile of all the linkages investigated. Comparison of activation energies and binding affinities to the sodium cation revealed an increase in activation energy in proportion to the increment in binding affinity. The calculated stabilities of glycosyl bonds were: α-Man (Manα1 → 3, 4 or 6Man) > β-Gal (Galβ1 → 4Gal) > α-GalNAc (GalNAcα1 → 4GalNAc) > β-Man (Manβ1 → 4GlcNAc) > α-Gal (Galα1 → 3, 4 or Gal) > β-Man (Manβ1 → 4Man) > β-GalNAc (GalNAcβ1 → 4GalNAc) > α-Fuc (Fucα1 → 6GlcNAc) > α-Fuc (Fucα1 → 4GlcNAc) > β-GlcNAc (GlcNAcβ1 → 4GlcNAc) > α-Fuc (Fucα1 → 3GlcNAc) > α-NeuNAc (NeuNAcα2 → 3 or 6); this result was close to the experimentally deduced trend.

A. In-Source Decay (ISD)

In-source decay frequently accompanies ionization of permethylated glycans. Although the presence of fragments can lead to complex spectra, they can also be used to obtain pseudo-MS^3 spectra. Smargiasso and De Pauw (2010) have investigated matrices and conditions for optimal production of such ions and have concluded that DHB was the most versatile matrix; the presence or absence of ISD fragments could be controlled, depending on the location of the laser shots. Spectra obtained from the center of DHB targets produced mainly $[M+Na]^+$ ions that did not yield ISD fragments, whereas spectra from the crystals surrounding the target yielded mainly $[M+H]^+$ ions that fragmented readily. 9-AA (6/18), on the other hand, formed homogeneous matrix spots and did not induce ISD.

Soltwisch and Dreisewerd (2010) have noted that collisional cooling in an orthogonal TOF mass spectrometer stabilizes fragment ions that are generated in-source and that by varying the buffer gas pressure, production of ISD and post-source (PSD)-type ions could be varied. Under high-pressure conditions, ISD-type fragments of *O*-linked glycosylated peptides were generated that retain the glycan. PSD fragments, on the other hand, showed partial loss of the glycan from y-type peptide fragments.

B. PSD

The detailed positive ion PSD and ISD fragmentation of deprotonated D-ribose (**1/1**) and D-fructose (**1/16**) has been studied with the aid of the isotopically labeled analogues, [1-^{13}C]-D-ribose, [5-^{13}C]-D-ribose and [C-1-^{2}H]-ribose (Bald et al., 2009). The fragmentation was compared with fragmentation through dissociative electron attachment (DEA). Fragmentations of deprotonated monosaccharides formed in the MALDI process, as well as their transient molecular anions formed upon electron attachment, were characterized by loss of different numbers of H_2O and CH_2O units. Two different fragmentation pathways leading to cross-ring cleavage were identified. Metastable decay of deprotonated D-ribose proceeded either *via* an X-type cleavage yielding fragment anions at $m/z = 119$, 100, and 89 (dominant ion, $C_3H_5O_3$), or *via* an A-type cleavage resulting in $m/z = 89$, 77 and 71. This result is in contrast to previous CID studies where only A-type cross-ring cleavage was proposed. It was found that the heavier fragment anions at $m/z = 119$ and $m/z = 100$ generated *via* metastable decay exclusively arise from an X-type cleavage whereas the smaller fragment anions at $m/z = 89$ and 71 arise predominantly from an A-type cleavage. A fast and early metastable cross-ring cleavage of deprotonated D-ribose observed in ISD was dominated by X-type cleavage leading mainly to $m/z = 100$ and 71; the latter ion is not the same as that found in PSD. For DEA of D-ribose, a sequential dissociation was identified that included metastable decay of the dehydrogenated molecular anion leading to $m/z = 89$. The most dominant fragment ions in DEA were due to faster decompositions occurring within several hundred nanoseconds (as in ISD) and, thus, sequential reactions including an initial dehydrogenation could be excluded.

Several oligosaccharides (aldoses) and oligosaccharide alditols derived from agaroses, κ- and ι-carrageenans obtained by hydrolysis of agaroses and carrageenans, two important types of red seaweed polysaccharides, have been used as model compounds to study prompt (ISD) and PSD fragmentation. Sulfated alditols gave $[M-H]^-$ ions in negative-ion mode together with prompt fragment ions produced mainly by desulfation. Sulfated aldoses gave mainly prompt fragmentation ions (C-cleavages and desulfation). Non-sulfated aldoses and alditols only gave ions ($[M+Na]^+$) in positive ion mode with no prompt fragmentation. The aldoses yielded cross-ring fragmentation in the PSD mode. Several different matrices (DHB, *nor*-harmane (**1/35**), ferulic acid (**1/41**) and the ionic liquid matrices DHB/acid-*n*-butylamine and ferulic acid/*n*-butylamine) were investigated; the best results were obtained with DHB and *nor*-harmane (Fatema et al., 2010).

C. CID

CID on TOF/TOF and magnetic sector instruments have been compared with several types of biomolecule (Pittenauer & Allmaier, 2009). The sector instruments produce high-energy collisions (8–20 keV) yielding more structural information from

many compounds than instruments producing only low energy (1 keV) collisions. The case with different TOF/TOF instruments is less clear-cut because the collision energy is spread over a wide range. Fewer differences were seen with carbohydrates than with some other compound types because most fragmentations (except formation of X-type cross-ring cleavages) occur at low energies. High-energy fragmentation in positive ion mode generally enhanced the relative abundance of cross-ring cleavage fragments, particularly X-type ions and has been used with HPLC (offline) to provide a powerful method for glycoprotein analysis (Tryfona & Stephens, 2010). Full experimental details are given in the paper.

D. Photofragmentation

Experimental details for obtaining infrared multiphoton dissociation (IRMPD) spectra from carbohydrates have been described (Li et al., 2009a). The technique offers the advantage that, because both parent and product ions can absorb IR photons, the spectra can be richer in information than those obtained by CID. In the same publication, the authors discuss sustained off-resonance irradiation-collision-induced dissociation (SORI-CID) implemented with a MALDI-FT-ICR mass spectrometer which produced similar spectra to IRMPD. Experimental details are described. SORI-CID with MALDI-FT-ICR has also been applied to MUC-type *O*-glycans (Li et al., 2009b).

The 157 nm photodissociation of *N*-linked glycopeptides has been investigated in a modified MALDI TOF/FOF instrument by irradiating the ions within the collision cell. Singly charged glycopeptide ions from horseradish peroxidase (HRP) yielded abundant peptide and glycan fragments. The peptide fragments included a series of x-, y-, v-, and w-ions with the glycan remaining intact. These ions provide information about the peptide sequence and the glycosylation site. The glycan fragmented to give both glycosidic fragments and abundant cross-ring fragments that were not observed in low-energy CID spectra. Doubly charged glycopeptides generated by nanospray in a linear IT mass spectrometer also yielded peptide and glycan fragments. However, the former were dominated by low-energy fragments such as b- and y-type ions while the glycan was primarily cleaved at glycosidic bonds (Zhang & Reilly, 2009).

E. Multiple Successive Fragmentation (MS^n)

MALDI-LIFT-TOF-MS/MS and ESI tandem mass spectrometry (ESI-IT-MS/MS^n) have been used for the characterization of free oligosialic acids and those derivatized with DMB, as well as partially *O*-acetylated derivatives. Electrospray required the acids to be lactonized but the larger lactones could only be detected by MALDI-TOF. The fragmentation spectra were dominated by simultaneous cleavage of glycosidic linkages and the corresponding lactone ring, whereas classical cross-ring fragments were of minor abundance. However, the combined use of the two different types of fragmentation analysis allowed a sensitive and detailed characterization of both short- and long-chained species. Furthermore, oxidation of the nonreducing end sugar moiety enabled sequence determination and localization of acetylated and nonacetylated sialic acid residues (Galuska et al., 2010a).

The effect of the pressure of cooling gas in the ion source of an orthogonal-TOF MS has a strong influence on the extent of analyte ion fragmentation. Soltwisch et al. (2009) have investigated the effect of this parameter on peptide and oligosaccharide fragmentation using substance P and the milk sugar, LNFP-II (**52**), respectively in both UV- and/or IR-MALDI. A range of pressures, from 0.05 to 1.8 mbar was used in combination with seven different buffer gases (He, Ne, Ar, N_2, CO_2, CH_4, and isobutane). The influence of the ion extraction voltage on the analyte fragmentation was also investigated for a selected set of gas parameters. Fragment ions exhibited characteristic fragment yield-pressure dependencies that were classified into three groups. For LNFP-II, the yield of molecular ions rose with pressure until at the higher pressures, it was similar to that from substance P. The authors speculated that the consistently lower ion yields reported from oligosaccharides could be attributed to the generally low pressures used when recording their spectra. With respect to fragmentation, glycosidic fragment ions (termed Type I) ions dominated the spectra at low pressure but their relative abundance fell dramatically as the pressure rose. The ions resembled species that are also found in MALDI-PSD MS. The abundance of type II ions, which resembled typical ISD fragments, and consisted mainly of cross-ring products, rose with pressure, probably because of a reduction in the secondary fragmentation process that resulted in loss of fucose. A few other ions, termed type III ions did not show such dramatic changes with pressure. Comparing the yields of fragmentation for the different buffer gases revealed a correlation between their internal degrees of freedom and their collisional cooling efficiency. Changing the buffer gas pressure and/or extraction field provided an easy means to influence analyte ion fragmentation and to switch from the primary production of one type of fragment species to another.

LNFP II, **52**

F. Internal Residue Losses

Hexose rearrangements of protonated molecules of *N*-glycopeptides and reductively aminated *N*-glycans have been observed by MALDI-TOF/TOF-MS/MS and ESI-IT-MS/MS (Wuhrer, Koeleman, & Deelder, 2009b). Fragmentation of proton adducts of 2-AB and 2-AA-labeled high-mannose *N*-glycans from RNaseB resulted in transfer of one to five Hex residues to the fluorescently labeled innermost GlcNAc residue. Glycopeptides from various biological sources containing high-mannose glycans were likewise shown to undergo Hex rearrangement reactions, resulting in migration of one or two Hex moieties to the chitobiose core. Tryptic Fc-glycopeptides from IgG peptides containing biantennary *N*-glycans were also shown to undergo Hex rearrangements. Such rearrangement products can cause major problems with the interpretation of unknown glycans but, fortunately, do not appear to occur from $[M+Na]^+$ ions, the major ions in MALDI spectra of most neutral carbohydrates.

X. COMPUTER ANALYSIS OF SPECTRA

The use of computer software for analyzing carbohydrate spectra is not as advanced as that for proteins; nevertheless,

many investigators have developed software for spectral interpretation, composition calculations, and have constructed databases, usually for specific glycan types. Much of this software is applicable to spectra generated from the majority of common ion sources. A good source of information is the book *Bioinformatics for Glycobiology and Glycomics: An introduction* by the late Claus-Wilhelm von der Lieth, Luetteke, and Frank (2009). In addition, various tools for glycomics and available databases are covered in a comprehensive review by Frank and Schloissnig (2010).

A. Algorithms for Analyzing Spectra

The simplest of these algorithms calculates compositions from *m/z* values. Although such software is extremely valuable, a composition is not a structure and such programs should not be used as the basis of labeling spectra unless the proposed structures are confirmed by suitable techniques. One such tool reported in the review period is called lipID and calculates molecular compositions for glycerophospholipids, GSLs, fatty acids and small oligosaccharides from *m/z* values entered as single values or as mass lists. The user-extendable software is a Microsoft Excel Add-In developed using Visual Basic for Applications and is compatible with all Versions of MS Excel since MS Excel 97 (Hübner, Crone, & Lindner, 2009).

Kronewitter et al. (2009) have constructed a library of possible *N*-glycan masses by successive dismantling of tetra-antennary hybrid and high-mannose glycans. These calculations gave the possible masses that would be expected in a glycan mixture. Three hundred thirty one distinct neutral compositions were obtained but many of these will represent several isomeric glycans. The smallest mass difference that was observed was 0.37 Da. However, many of the masses coincided with isotope peaks from ions of different compositions meaning that, without deisotoping, a resolution of at least 12,500 would be needed to resolve all peaks. The theoretical masses were matched against measured masses from *N*-glycans released from human serum glycoproteins and 78 discrete compositions were detected.

In a similar way, an *in silico* glycan database of possible *N*-glycan compositions has been constructed by addition of known monosaccharide residues, such as those in a Neu5Ac-Gal-GlcNAc antenna, to the common trimannosyl chitobiose core. The derived masses were then matched to the experimental mass and the software, named Glyquest, predicted compositions and possible structures. Next, it calculated possible glycosidic fragments from the proposed structures, matched these to the experimental mass spectrum and constructed a spectrum labeled with the proposed structures (Gao, 2009). The software could also be applied to glycans containing fluorescent labels such as 2-AB but was not applicable to glycopeptides with unknown modifications. However, as with much of the software developed for this work, the detailed structural details such as the linkage of each monosaccharide are not available and the software must be regarded as a guide to the total structure. A similar "branch-and-bound" algorithm developed by Peltoniemi, Joenväärä, and Renkonen (2009) starts with the trimannosyl-chitobiose core and then constructs *N*-type glycans in an iterative process until the target carbohydrate composition is reached. The algorithm identified several glycans from TF and human serum samples.

GlycoSpectrumScan is a web-based tool that identifies the glycoheterogeneity on a peptide from mass spectrometric data. Two experimental data sets are required as inputs: (1) oligosaccharide compositions of the *N*- and/or *O*-linked glycans present in the sample and (2) *in silico* derived peptide masses of proteolytically digested proteins with a potential number of *N*- and/or *O*-glycosylation sites. GlycoSpectrumScan uses MS rather than MS/MS data, to identify glycopeptides and determine the relative distribution of *N*- and *O*-glycoforms at each site. It can be used to assign monosaccharide compositions on glycopeptides with either single or multiple glycosylation sites. The algorithm allows the input of raw mass data, including multiply charged ions, making it applicable for both ESI and MALDI data from all mass spectrometer platforms. Low resolution data from, for example, ITs are heavily smoothed to yield the average mass whereas data from high resolution instruments receive a milder smooth and deisotoping to give the monoisotopic mass. The software was used to characterize the *N*- and *O*-linked glycopeptides from human secretory IgA (sIgA), consisting of secretory component (7 *N*-linked sites), IgA1 (2 *N*-linked, $\leq$5 *O*-linked sites), IgA2 (4 *N*-linked sites) and the J-chain (1 *N*-linked site). GlycoSpectrumScan is freely available at www.glycospectrumscan.org (Deshpande et al., 2010).

Prediction of glycosylation sites is another area of software development. A program that predicts *N*- and *O*-glycosylation sites based on local information, general protein information, sub-cellular localization and binding specificity of glycosyltransferases has been developed and was claimed to be about 90% accurate (Sasaki, Nagamine, & Sakakibara, 2009a). However, as with all predictive programs that are not 100% accurate, results should only be taken as a guide for designing appropriate location experiments.

Software that attempts to predict structures from spectra is possibly the most active area in computer applications. SimGlycan® is one such tool (Apte & Meitei, 2010). The software accepts raw or standard experimental MS data files, matches them with its own database of theoretical fragments and generates a list of probable candidate structures. Each structure is scored to reflect how closely it matches the experimental data. The software also predicts novel glycan structures by drawing a glycan and mapping it onto the experimental spectrum. Other biological information is also available for easy reference. The program can be downloaded from http://www.premierbiosoft.com/glycan/index.html.

Another software platform for carbohydrate assignment is SysBioWare, developed by Vakhrushev, Dadimov, and Peter-Katalinić (2009) and designed to work directly from raw MS data. The data are first imported into the spectrum browser, baseline corrected and denoized. Peak detection is based on shape matching and the software detects monoisotopic *m/z* values and charge states. A biological filter is used during compositional analysis of the monoisotopic ions. The software was successfully tested with human urine.

SysBioWare, a software platform developed for MS data evaluation in glycomics, has been applied to the interpretation of spectra from human serum GSLs. The masses of predicted ions arising from cleavages in the glycan and the ceramide moieties were calculated, thus enabling structural characterization of both entities. The calculated masses were then used to

match with those in the spectra for structural identification (Souady et al., 2010).

Böcker, Kehr, and Rasche Böcker (2009) have presented an algorithm for calculating glycan structures from tandem mass spectra. Twenty-four spectra (of $[M+H]^+$ ions) of 2-AP-labeled *N*-glycans obtained from batroxobin (from *Bothrops moojeni* venom) were used as test compounds, The spectra were measured with a TOF/TOF instrument with a MALDI ion source and the algorithm rapidly predicted possible topologies. Biological restraints needed to be used to limit the predictions to reasonable structures.

Goldberg et al. (2009) have compared three algorithms, "Max Subgraph," "Parsimony," and "RandomWalk" that make inferences about glycan synthesis from biological knowledge for their ability to assign structures from 71 single-MS spectra from a variety of tissues and organisms, containing more than 2,800 manually annotated peaks. Max Subgraph behaved better than the other two but only uniquely assigned the correct structure to about half of the peaks in 41 out of the 71 spectra.

A computer model that predicts *N*-linked glycan profiles based on cellular enzyme activities has been developed (Krambeck et al., 2009). The paper describes the expansion of a previously developed detailed model for *N*-linked glycosylation (Krambeck & Betenbaugh, 2005) with the further application to analyze MALDI-TOF mass spectra of human *N*-glycans. The glycosylation reaction network is automatically generated by the model, based on the reaction specificities of the glycosylation enzymes and allows prediction of the complete glycan profile and its abundances for any set of assumed enzyme concentrations and reaction rate parameters. A predicted mass spectrum of model-calculated glycan profiles is obtained and enzyme concentrations are adjusted to bring the theoretically calculated mass spectrum into agreement with that obtained experimentally. The result is a complete characterization of a measured glycan mass spectrum containing hundreds of masses in terms of the activities of 19 enzymes. In addition, a complete annotation of the mass spectrum in terms of glycan structure is produced, including the proportions of isomers within each peak. The method was applied to mass spectrometric data obtained from normal human monocytes and monocytic leukemia (THP1) cells.

A kinetic model originally developed for the prediction of peptide CID spectra has been extended to predict the CID spectra of *N*-glycopeptides. The model was trained with 1831 CID spectra obtained with an ion trap and was able to predict CID spectra with excellent accuracy in ion intensities for *N*-glycopeptides up to 8,000 Da in mass. The program is said to be capable of predicting up to 524 common glycoforms including high-mannose, hybrid and complex *N*-glycans with two to four antennae (Zhang & Shah, 2010).

Spencer et al. (2010) have devised a computational approach to predict the fine structure and patterns of domain organization of heparan sulfate (HS). Analysis uses chemical composition data obtained after complete and partial enzymatic digestion of mixtures of HS chains and produces populations of theoretical HS chains with structures that meet both biosynthesis and enzyme degradation rules. The program was used to analyze HS from various cell types and good agreement was found between experimental data and computer predictions.

GlycoViewer (http://www.systemsbiology.org.au/glycoviewer) is a web-based tool that can visualize, summarize, and compare sets of glycan structures. It takes as its input a list of glycan structures in International Union of Pure and Applied Chemistry (IUPAC) format or glycan structures constructed with a sugar structure builder. The output is a graphic, which summarizes all salient features of the glycans according to features such as the nature and length of any chains and the types of terminal epitopes. The tool can summarize several hundred glycan structures in a single figure. The report contains an example of use of the tool for analysis of normal and disease associated glycans from the human glycoproteome (Joshi et al., 2010).

B. Databases

Several glycan databases are available. The kyoto encyclopedia of genes and genomes (KEGG) GLYCAN databases contain useful information on glycan structures and metabolic pathways (Hashimoto & Kanehisa, 2009) and data mining the Protein Data Bank for glycol-related data using the GLYCOSCIENCES.de internet portal has been discussed in *Methods in Molecular Biology* (Lütteke & von der Lieth, 2009). Ito et al. (2010a) have synthesized *N*- and *O*-linked glycan libraries (named Glycan Mass Spectral Database, GMDB) and constructed a library of their positive ion MS^2, MS^3 and MS^4 fragmentation spectra. *N*-Glycans were in the form of their 2-AP derivatives whereas *O*-glycans that were released by β-elimination were not. The library was said to be accessible on-line at http://riodbdev.ibase.aist.go.jp/rcmg/glycodb/Ms (However, attempts by the reviewer to connect to the site have failed.) It can be searched either by MW of glycan composition in terms of isobaric monosaccharides and instructions on how to use the software are given in the paper.

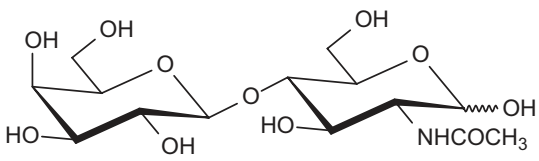
Although such databases and tools for glycomics are readily available on the web, these have, until now, been isolated. This unfavorable situation has been discussed (von der Lieth, 2007) and has been largely overcome by Ranzinger et al. (2009) who have developed GlycomeDB, a meta-database for public carbohydrate sequences. At the time of publication (2009) it contained 35,056 unique structures in GlycoCT (www.glycome-db.org) encoding, referencing more than 100,000 external records from 1,845 different taxonomic sources. A user-friendly, web-based graphical interface has been developed which allows taxonomic and structural data to be entered and searched. The structural search possibilities include substructure search, similarity search, and maximum common substructure. A novel search refinement mechanism allows the assembly of complex queries. With GlycomeDB, it is now possible to use a single portal to access all digitally encoded, public structural data in glycomics and to perform complex queries with the help of a web-based user interface. A list of databases is given in Aoki-Kinoshita (2010).

C. Tools for Displaying Structures

N- and *O*-glycan structures are usually depicted with small cartoons in which each constituent monosaccharide is shown by a symbol. Unfortunately, there is no consensus on which symbol to use for any particular monosaccharide with most investigators preferring to develop their own system. Several years ago, the Consortium for Functional Glycomics (CFG) attempted to redress the problem with the introduction of a system that has

since been adopted by several laboratories. Unfortunately, this system has several major drawbacks: (a) it does not diagrammatically show linkage or anomericity and (b) it uses color to differentiate hexoses, thus causing problems when structures are printed in black and white and making the system difficult to use with pen or pencil on paper. A new system that overcomes these problems has recently been introduced (Harvey et al., 2009c). Monosaccharides are shown as shapes with various additions to indicate functional groups (e.g. an inclusive dot to indicate a deoxy-sugar and a filled shape to code for an *N*-acetyl sugar). Linkage is shown by the angle of the lines linking the sugar symbols and anomericity is shown by the type of line (full for a β-bond and broken for an α-link). Examples can be seen below. Although color is not used to define monosaccharides, the CFG colors can be used with the Oxford symbols. Unfortunately, color was omitted from the table of symbols in the original article but was published later as an erratum (Harvey et al., 2009b). The article received comments from the authors of the CFG system (Varki et al., 2009) and discussion is continuing. This scheme and others are compared in a review by Frank and Schloissnig (2010).

Two tools for displaying *N*-glycans found in the mammalian CHO cell line have been developed (McDonald et al., 2010). Both take as input the 9-digit identifier devised by Krambeck and Betenbaugh (2005) that uniquely defines each structure assuming the existence of the trimannosyl-chitobiose core. The first of these tools, GlycoForm, is designed to display a single structure from an identifier entered by the user. The display is updated in real time, using symbols for the sugar residues, or in text-only form. The two symbol sets discussed above are used, the symbols and layout devised by the CFG http://www.functionalglycomics.org/static/consortium/Nomenclature.shtml or the alternative "Oxford" system used by Glycobase, a relation database of 2-AB labeled *N*-glycans (Campbell et al., 2008). However, although GlycoForm can display structures using the Oxford system, unfortunately, it does not display the correct linkage information that is inherent to the full Oxford system. In addition, GlycoForm can display the name of the glycan as used by Glycobase. GlycoBase formalism does not yet handle *N*-acetyllactosamine (NAcLac, **53**) repeating units and is, therefore, currently limited to structures with one Gal residue per branch. Structures can be added to a library, which is recorded in a preference file and loaded automatically. Individual structures can be saved as image files either Portable Network Graphics (PNG), JPEG or Windows Bitmap (BMP) formats. The second program, Glycologue, reads a file containing columnar data of nine-digit codes, which can be displayed on-screen and printed at high resolution. Both programs, for Windows, Mac OS X and Linux x86 GTK can be downloaded from http://www.boxer.tcd.ie/gf.



N-Acetyllactosamine (**53**)

XI. STUDIES ON SPECIFIC CARBOHYDRATE TYPES

A. Mono- and Oligosaccharides

A major problem with the analysis of monosaccharides or small oligosaccharides by MALDI is the presence of very abundant ions from matrices such as DHB in the low mass region of the spectra. Various methods for overcoming this disadvantage are discussed above. Nevertheless, MALDI with conventional matrices has produced results and the technique works well for the larger oligosaccharides. Thus, oligosaccharides from dextran, alginate, hyaluronan and chondroitin sulfate have been characterized by MALDI-TOF MS directly from a TLC plate after soaking it in the DHB matrix. The plate had a metal backing to ensure electrical contact. The TLC solvent system was *n*-butanol/formic acid/water (3:4:1, v/v/v). It was found that the high content of formic acid caused few problems but was responsible for partial formylation of glycosaminoglycans (GAGs) and minor *N*-acetyl loss from hyaluronan and chondroitin sulfate (Nimptsch et al., 2010).

A comparative study of MALDI and a new technique, electrospray droplet impact secondary ion mass spectrometry (EDI/SIMS) has been applied directly to fruits such as bananas, apples, grapes and strawberries. The major constituents, fructose (**1/16**), glucose (**1/4**), sucrose (**6**) and organic acids gave abundant $[M + K]^+$ ions positive mode and CF_3COO^- adducts in negative mode (the CF_3COO^- ions came from CF_3COOH in the ESI spray. These negative ion spectra were almost free of background ions. MALDI from DHB, on the other hand, although producing positive ions gave virtually no ionization in negative ion mode (Asakawa and Hiraoka, 2010).

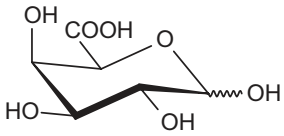
B. Polysaccharides

Reviews of the analysis of polysaccharides are listed in Table 5. Large polysaccharides need to be hydrolyzed, often enzymatically but sometimes chemically, to smaller fragments before they are amenable to MALDI analysis. One chemical method involves the selective cleavage of the Rha*p*-(1 → 4)-α-GalA*p* linkage in rhamnogalacturonans. Enzymic cleavage of this linkage is often ineffective, especially in highly branched rhamnogalacturonans but Deng et al. (2009) have developed an improved chemical fragmentation method based on β-elimination of esterified 4-linked galacturonic acid (Gal*p*A, **54**) residues that overcomes the problem. At least 85% of the carboxyl groups of the Gal*p*A residues in *A. thaliana* seed mucilage were converted to methyl or hydroxypropyl esters and β-elimination was found to be more extensive with hydroxypropyl-esterified than with methyl-esterified rhamnogalacturonans. The non-reducing 4-deoxy-β-l-*threo*-hex-4-ene-pyranosyluronic acid (**55**) residue formed by the β-elimination reaction was removed by treatment with aqueous *N*-bromosuccinimide. This method was used to fragment the branched rhamnogalacturonan from peppergrass seed mucilage with product characterization by MALDI-TOF MS, glycosyl residue composition analysis, and 1 and 2D NMR spectroscopy. The results showed that the most abundant low-MW fragments contained a backbone rhamnose (**1/10**) residue substituted at O-4 with a single side-chain, and suggest that peppergrass seed mucilage rhamnogalacturonans is composed mainly of the repeating unit 4-*O*-methyl-α-D-Glc*p*A-(1 → 4)-β-D-Gal*p*-(1 → 4)-

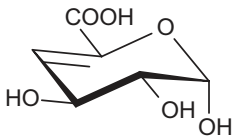
TABLE 5. Reviews on the Use of MALDI for the Analysis of Polysaccharides

Subject	Comments	Citations	Reference
Spectroscopic methods for structural analysis of chitin and chitosan	Several methods (IR, UV, NMR, X-ray, MS (MALDI, ESI etc.))	349	(Kumirska et al., 2010)
Characterization of branched polysaccharides using multiple-detection size separation techniques	Review of many techniques including MALDI	111	(Vilaplana & Gilbert, 2010)
Structure and analysis of pectins	Mainly a review of structure	144	(Voragen et al., 2009)
Analysis of pectins by mass spectrometry	Mainly fragmentation	116	(Ralet et al., 2009)
Structural analysis of starch and cellulose derivatives	Discusses methods for the determination of the average degree of substitution, monomer composition, and substitution patterns	-	(Mischnick & Momcilovic, 2010)
Structure and analysis of carrageenans	NMR, colorimetric methods, chromatography and MS	145	(Campo et al., 2009)

[→4)-α-D-Gal*p*A-(1→2)-]-α-L-Rha*p*-(1→.

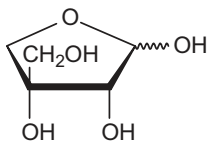


Galacturonic acid, **54**



4-Deoxy-β-L-*threo*-hex-4-enepyranosyluronic acid, **55**

Another chemical method for analysis of rhamnogalacturonan II makes use of mild acid hydrolysis to hydrolyze the acid-labile monosaccharides 3-deoxy-D-*manno*-oct-2-ulosonic acid (Kdo, **1/13**), 3-Deoxy-*D-lyxo*-2-heptulosonic acid (Dha) and apiose (Api, **56**) at the branchpoint between the sidechains and the oligogalacturonide backbone to release short polysaccharide chains that were analyzed by ESI and MALDI-TOF MS (Séveno et al., 2009). The method was optimized using citrus pectin and then applied to other plant species.



Apiose, **56**

Experimental details for examination of extracellular polysaccharides (EPSs) from plants following digestion with a variety of endoglycosiodases and MALDI-TOF analysis from DHB has been reported by Günl, Gille, and Pauly (2010). Other examples are listed in Tables 6 (plants) and 7 (bacteria).

C. Cyclodextrins and Related Compounds

Ionization efficiencies of cyclodextrins and corresponding linear compounds (maltohexaose and maltoheptaose) have been compared together with differences in the ionization efficiencies of α- and β-cyclodextrins (**4/6**) (Choi et al., 2009). Alkali metal salts of Li^+, Na^+, K^+, and Cs^+ were used as the cationizing agents to enhance the ionization efficiency. Relative ion intensities of the cyclodextrins were much larger than those of the linear carbohydrates and the difference showed an increasing trend with the size of the alkali metal cation. β-Cyclodextrin had higher ionization efficiency than α-cyclodextrin (**4/24**) and the difference increased with increasing size of the alkali metal cation. The ionization efficiency was also found to be affected by the counter anions. The higher ionization efficiencies of cyclodextrins were explained with the number of coordination sites and the binding energies.

D. Milk Sugars

Analysis of milk oligosaccharides appears to be receiving increasing attention. Reviews of mass spectrometric methods for their analysis have been published by Niñonuevo and Lebrilla (2009), Kolarich and Packer (2010) and Urashima et al. (2009). Wu et al. (2010b) have developed an annotated library of neutral human milk oligosaccharides with characterization by HPLC, MALDI-FT-ICR MS and exoglycosidase digestion.

Pyrene labeling (Amano et al., 2009a) has been used by Amano et al. (2009b) to enable neutral carbohydrates from human milk to be observed by negative ion MALDI-TOF MS^n. The neutral oligosaccharides from the milk of a woman (blood type A, Le^{b+}) were obtained by anion-exchange column chromatography after the removal of lipids and proteins. Further fractionation was performed by means of *Aleuria aurantia* lectin-Sepharose column chromatography and reversed-phase HPLC after labeling. Twenty-two oligosaccharides with decaose cores were identified and, of these 21 had novel structures.

TABLE 6. Use of MALDI MS for Examination of Carbohydrate Polymers From Plants and Animals

Species	Carbohydrate	Methods[1]	Notes	Reference
Abelmoschus esculentus (L.) Moench (Okra)	Cell wall polysaccharides	Polygalacturonase, pectin Me-esterase, TOF (DHB), GLC, GC/MS, NMR	Structural determination	(Sengkhamparn et al., 2009b)
Abelmoschus esculentus (L.) Moench (Okra)	Pectin	Various galactanases and galacturonases, TOF (DHB), ESI, NMR, SEC	Identification of unusual substitution of Rha residues with acetyl and alpha-linked Gal groups	(Sengkhamparn et al., 2009a)
Agave tequilana	Water-soluble carbohydrates	L-TOF (DHB), GC/MS	Investigation of fructans with age (2, 4, 6.5 years)	(Arrizon et al., 2010)
Allium cepa L. (Onion)	Fructooligo-saccharides	TOF (DHB)	Ident. of carbohydrates during storage	(Fujishima et al., 2009)
Amorphophallus konjac C. Koch	Konjac glucomannan	TOF/TOF (DHB)	Use of CE-LIF for analysis	(Albrecht et al., 2009)
Arabidopsis thaliana	Rhamno-galacturonan II	Mild acid hydrolysis, TOF (DHB)	Structural determination using acidic fingerprinting	(Séveno, et al., 2009)
Arabidopsis thaliana	Xyloglycans from cell walls	XyG-specific endoglucanase, TOF (DHB)	Structural determination and as illustration of MALDI-TOF profiling	(Obel et al., 2009)
Arabidopsis thaliana	β-Glucan	β-Glucan hydrolase, TOF	Barley cellulose synthase-like CSLH gene mediates (1,3;1,4)-β-D-glucan synth. in transgenic *Arabidopsis*	(Doblin et al., 2009)
Arabidopsis thaliana	Rhamno-galacturonan II	TFA, TOF (DHB), ESI, GLC	Characterization of putative Kdo transferase gene	(Séveno et al., 2010)
Arabidopsis thaliana	Oligosaccharides from leaves and hypocotyls	Pectinases, hemicellulases, and cellulases TOF/TOF (DHB)	MALDI-TOF MS and CE-LIF fingerprinting of digests as screening tool for cell wall mutants	(Westphal et al., 2010a)
Arabidopsis thaliana	Xyloglucans	Endocellulase, TOF (DHB)	Mutations lacking α-xylosidase activity alter xyloglucans and produce growth defects	(Sampedro et al., 2010)
Arabidopsis thaliana	Xylooligo-saccharides	β-Xylanase M6, TOF (DHB)	GT43 Glycosyltransferases shown to be essential for the elongation of glucuronoxylan backbone	(Lee et al., 2010b)
Arabidopsis thaliana	Oligo-galacturonides	TOF	Supramolecular conformation modulated by chitosan oligosaccharides	(Cabrera et al., 2010)
Arabidopsis thaliana	Xyloglucan	Endo-glucanase, TOF (DHB)	Characterization of pollen tube cell wall	(Dardelle et al., 2010)
Arabidopsis thaliana	Acidic oligoxylans from stems	Endoxylanase, TOF	Study of genes involved in cell wall synthesis	(Minic et al., 2009)
Arabidopsis thaliana	Glucuronoxylan (GX)	β-Xylanase, TOF (DHB/HIQ)	F8H and FRA8 genes shown to be functional paralogs and to function redundantly	(Lee et al., 2009d)
Arabidopsis thaliana	Glucuronoxylan (GX)	Xylanase Xyl10A, TOF/TOF (DHB), glycans (Per-$^2H_3$-Me)	IRX10 and IRX10-like genes shown to be essential for GX biosynthesis	(Brown et al., 2009)
Arabidopsis thaliana	Oligo-galacturonides (OGs)	Pectinase, TOF/TOF (CHCA)	Plant immunity induced by OGs shown to alter root growth by involving flavonoid accumulation	(Hernández-Mata et al., 2010)

TABLE 6. (*Continued*)

Arabidopsis thaliana with *MUR*3 gene from *Eucalyptus grandis*	Xyloglucans	Xyloglucan-specific endo-β-1,4-glucanase, R-TOF	Gene shown to encode a galactosyltransferase	(Lopes et al., 2010a)
Arctium lappa L. (Burdock)	Reducing fructooligo-saccharides	TOF (DHB), GLC	Isolation and structural determination	(Ishiguro et al., 2009)
Beta vulgaris (Sugar beet)	Branched arabino-oligo-saccharides	*C. lucknowense* arabinohydrolases, TOF (DHB)	Isolation and identification	(Westphal et al., 2010b)
Beta vulgaris L. (Sugar beet)	Polysaccharides from pulp	R-TOF/TOF (DHB)	Use of introduced ion-exchange groups to extract polysaccharides in high yield	(Šimkovic et al., 2009)
Brassicaoleracea var. Capitata, Bartolo cultivar (White cabbage)	Pectin	β-Elimination, TOF/TOF (DHB), glycans (per-Me)	Release and characterization of single side chains	(Westereng et al., 2009)
Brassica napus (canola) *Triticum aestivum* (wheat) *Chara corallina*, (cytoplasm)	*bis*-Sucrose borate	R-TOF (3-AQ)	Identification of low molecular weight boron complexes (*bis*-sucrose borate). Mechanism of boron mobility	(Stangoulis et al., 2010)
Cornus officinalis (Dogwood)	Polysaccharide FCAP1	Endo-β-D-glycanase, TOF (DHB), GLC, GC/MS	Isolation and structural determination (Glc, Man, Ara)	(Yang et al., 2010e)
Crab shells	Chitin oligo-saccharides	HCl, TOF	Production of chitin oligosaccharides with different MW and antioxidant effects	(Ngo et al., 2009)
Fleurya aestuans (West Indian woodnettle)	XXXG and XXGG Polysaccharides	TOF (DHB)	Structural characterization	(Angone et al., 2009)
Ganoderma lucidum (Mushroom)	Polysaccharide	TOF	Shown to enhance repair of radiation-induced damage to DNA from human cells	(Pillai et al., 2010)
Ganoderma lucidum (Mushroom)	β-Glucans	TOF	Conditions for recovery of water-soluble compounds by hydrothermal treatment	(Askin et al., 2010)
Hardwood kraft pulp	Neutral + acidic xylooligo-saccharides	*Trichoderma reesei* xylanase, QIT-TOF (DHB)	Structural analysis and utilization by intestinal bacteria *in vitro*	(Ohbuchi et al., 2009)
Hibiscus cannabinus (Kenaf)	Aldouronic acids	Endoxylanase, MALDI, glycans ($^2H_3$-Per-Me)	Structural determination and structures of alduronic acids liberated by endoxylanases	(Komiyama et al., 2009)
Hordeum vulgare L. (Barley)	Various carbohydrates	Carbohydrases and peptidases, TOF (DHB)	Experiments on enzymatic solubilization of brewers' spent grain	(Treimo et al., 2009)
Litchi chinensis (Lychee)	Pectins and fucosylated xyloglucans	Xylanase, glucanase, mannanase, TOF (DHB), GC/MS	Structural determination from cell walls of pericarp	(Hsieh & Wong, 2010)

(*Continued*)

TABLE 6. (*Continued*)

Nicotiana tabacum (Tobacco)	Xyloglucan from nectar	Fungal endoglucanase, TOF (2,4-DHB)	Interaction of Nectarin 4 with fungal protein shown to trigger microbial surveillance and defence mechanism	(Harper et al., 2010)
Oryza sativa (Rice)	Starch	*Thermus aquaticus* 4-α-glucanotransferase, TOF (DHB)	Structural modification and characterization of rice starch treated by *Thermus aquaticus* 4-α-glucanotransferase	(Cho et al., 2009d)
Oryza sativa (Rice)	Xylan, xyloglucan	Xylanase and xyloglucanase	Identification of Golgi-located type II membrane protein required for cell-wall biosynthesis	(Zhou et al., 2009b)
Oryza sativa (Rice)	Xylooligo-saccharides	Hydrothermal, Xylanase, TOF/TOF (DHB)	Manufacture and structural characterization of high-purity XOS by physicochemical processing of rice husks. Fermentation by fecal inocula	(Gullón et al., 2010)
Panicum virgatum var Alamo (Switchgrass)	Arabinoxylans	Endoxylanase, TOF (DHB), ESI, GC/MS, NMR	Structural analysis of arabinoxylans isolated from ball-milled biomass	(Mazumder & York, 2010)
Phaseolus vulgaris (Common bean)	Xyloglucan	Xyloglucan-specific endoglucanase, TOF (DHB)	Study of xyloglucan plasticity during habituation and dehabituation to lethal concentration of dichlobenil	(Alonso-Simón et al., 2010)
Phragmenthera capitata	XXXG Polysaccharides	TOF (DHB)	Structural characterization	(Angone, et al., 2009)
Pleurotus ostreatus (Mushroom)	α-(1→4)-glucans	R-TOF (DHB), GLC, GC/MS	Study of solubilisation of protein hydrophobin Vmh2 by glucans	(Armenante et al., 2010)
Pleurotus pulmonarius (Mushroom)	Polysaccharides	TOF (DHB), glycans (2-AB)	Chemical characterization, antiproliferative and antiadhesive properties of polysaccharides	(Lavi et al., 2010)
Populus alba × *tremula* (Poplar)	Glucuronoxylan (GX)	β-Xylanase, TOF (DHB/HIQ)	Down-regulation of PoGT47C expression shown to reduce GX increase wood digestibility by cellulase	(Lee et al., 2009e)
Populus tremuloides (Aspen) and corn stover	Heteroxylans	β-endoxylanase from *Aspergillus niger*, L-TOF (DHB)	Extraction and structural determination	(Naran et al., 2009)
Pseudotsuga menziesii (Douglas fir)	Oligo-galacturonans	TOF, TOF/TOF (DHB)	Aminated oligo-galacturonans grafted onto Douglas fir barks. For heavy metal removal	(Astier et al., 2010)
Rubus fruticosus and *Tamarindus indica*	Xyloglucan	TOF (DHB), HPLC	Enthalpic studies of xyloglucan-cellulose interactions	(Lopez et al., 2010)
Salvia (S. *miltiorrhiza* (SM), *S. sclarea* (SS) and *S. viridis* (SV))	Acidic β-(1→4)-xylans	H_2SO_4, TOF/TOF (DHB), CID	Structural determination of alkali-soluble hydrogels	(Yudianti et al., 2010)
Solanum lycopersicum L. cv West Virginia 106 (Cherry tomato)	Galacto-glucomannans	1,4-β-D-Mannanase, TOF, LC-MS, GC/MS	GDP-D-mannose 3,5-epimerase plays key role at the intersection of ascorbate and non-cellulosic cell-wall biosynthesis in tomato	(Gilbert et al., 2009)

TABLE 6. (*Continued*)

Solanum tuberosum (Potato)	Glucuronic acid oligomers	R-TOF/TOF	TEMPO oxidation of potato starch gives acid-resistant blocks of glucuronic acid	(ter Haar et al., 2010a)
Tamarindus indica (Tamarind)	Xyloglucans From seed	TOF (DHB)	Preparation of transparent film for various uses	(Simi & Abraham, 2010a)
Triticum spp. (Wheat)	Arabinogalactan protein	Protein-specific enzymes, TOF/TOF (DHB), glycans (per ^{13}C, ^{12}C-Me)	Structural analysis. Revision from earlier analyses	(Tryfona et al., 2010)
Commercial	Galacto-oligo-saccharides	FT-ICR (DHB), IRMPD	MALDI to analyse galacto-oligosaccharide syrup and to determine consumption by four major *bifidobacterial* phylotypes,	(Barboza et al., 2009)
Commercial	Sodium alginate	Hydrothermal, TOF, NMR	Investigation of depolymerization under hydrothermal conditions	(Aida et al., 2010)
Commercial	Galacto-oligo-saccharides	FT-ICR	Study of growth by different bifidobacteria	(Barboza, et al., 2009)
Commercial	Galacto-oligo-saccharides	TOF	For evaluation of CE-LIF as a potential analysis and quantification tool	(Albrecht et al., 2010)
Commercial	α-, β-, γ-Cyclodextrins	R-TOF/TOF (DHB)	For measurement of hydrodynamic properties of CD molecules	(Pavlov et al., 2010)
Various commercial	Carrageenans	Mild acid, TOF (1,2-diamino-4,5-methylene dioxybenzene)	Hydrolysis leads to complete series of odd-numbered oligosaccharides	(Yang et al., 2009a)
Various commercial	Methyl cellulose	Endoglucanase, TOF, glycans (Per-$^{2}H_3$-Me)	To test if enzymes can be used to determination heterogeneity of the substituent distribution	(Adden et al., 2009)
Various commercial	Carboxymethyl cellulose	Endoglucanase from *Trichoderma reesei*, TOF, LC/MS, glycans (per-Me)	To investigate selectivity of endoglucanases	(Enebro et al., 2009a)
Various commercial	Chitosans	TOF (DHB), Smith degradation, Bu esters	Deacetylated, water-soluble products examined as substrates for chitinase	(Yang et al., 2010a)
Various monocotyledons	Xyloglucans	Xyloglucan-specific endo-(1→4)-β-glucanase, TOF (DHB)	Structural determination - monocotyledons little studied. Have diverse structures	(Hsieh & Harris, 2009)
Maize (Commercial sample)	Starch	Solubilized with NaOH. Debranched with *iso*-amylase, TOF/TOF (DHB, CHCA)	Effect of acid dextrinization. Enzyme-resistant starch with linear chains with a maximum DP of 30 isformed under most conditions	(Htoon et al., 2010)
Zea mays (Maize, corn cob)	Hemicellulose	Hydrothermal, L-TOF (DHB)	Development of continuous flow type hydrothermal reactor for hemicellulose fraction recovery	(Makishima et al., 2009)
Unspecified, from aerobic granular sludge in municipal sewage	Alginate-like exopoly-saccharides	TOF, glycans (deacylated)	Polymers suggested to play a significant role in giving sludge with a highly hydrophobic, compact, strong and elastic structure.	(Lin et al., 2010e)

[1]Format (not all items present): Depolymerization method, MALDI method (matrix), compounds run (derivative), other methods.

TABLE 7. Use of MALDI MS for Examination of Carbohydrate Polymers From Lower Organisms

Species	Carbohydrate	Techniques[1]	Notes	Reference
Aspergillus fumaiatus	β(1→6)-branched β(1→3)-gluco-oligosaccharides	Endo β(1→3)-glucanase, TOF, GC/MS	Characterization of a new β(1→3)-glucan branching activity	(Gastebois et al., 2010)
Azotobacter sp. SSB81	Extracellular polysaccharide	TOF (DHB)	Enhanced production and partial characterization of the polysaccharide	(Gauri et al., 2009)
Bacillus anthracis	Cell wall polysaccharides	R-TOF/TOF (CHCA), ESI, NMR	Surface-layer proteins found to assemble by binding to secondary cell wall polysaccharide	(Kern et al., 2010)
Escherichia coli K5	Capsular polysaccharide	R-TOF	Capsular polysaccharide shown to confer virulence to *E. coli* K5 by being a 3D molecular mimetic of host heparin sulphate	(Blundell et al., 2009)
Francisella tularensis	Capsular polysaccharide	MALDI (DHB), GC/MS, NMR	Structural determination and studies on immunogenicity	(Apicella et al., 2010)
Fucus evanescens (Brown alga)	Fucoidan	Solvolysis, TOF (DHB), ESI	Linear polymer with alternating (1→3)- and (1→4)-linked fucose residues, sulfonated mainly at O-2 and partially acetylated	(Anastyuk et al., 2009)
Laminaria cichorioides (Brown alga)	Highly sulfated fucan	Auto-hydrolysis, TOF/TOF (DHB), ESI	Structural analysis by MALDI-TOF and ESI MS	(Anastyuk et al., 2010)
Mycobacterium marinum MMAR 2380	Lipo-arabinomannan	TOF	Predicted transmembrane acyltransferase shown to be essential for the presence of the mannose cap	(Driessen et al., 2010)
Mycobacterium tuberculosis	Lipo-arabinomannan and lipomannan	Proteinase K, TOF (CHCA), GC/MS	Inactivation of Man-transferase pimB shown to reduce cell wall lipoarabinomannan and lipomannan content and to increase rate of cell death	(Torrelles et al., 2009)
Pleurotus ostreatus (Mushroom)	α-(1→4)-cyclic glucans	L-, R-TOF (DHB, CHCA)	Interactions of protein hydrophobin Vmh2	(Armenante, et al., 2010)
Pseudomonas syringae pv. syringae	Osmoregulated periplasmic glucans	TOF (DHB), NMR	Novel anionic glucans with one succinyl residue at the C-6 position of Glc, plus neutral glucans up to DP 28	(Cho et al., 2009b)
Raoultella terrigena Ez-555-6	Exo-polysaccharide	TOF, NMR	From Chernobyl exclusion zone. Substituted with lactyl ether group	(Pillon et al., 2010)
Rhizobium tropici	NOD factors	Q-TOF	Many new NOD factors produced by high NaCl	(Estévez et al., 2009)
Saccharomyces cerevisiae	β-(1,6)-Glucan	Released by β-(1,3)-glucanase, TOF (DHB), GC/MS	Structural characterization and *in situ* synthesis. Cell wall glucan	(Aimanianda et al., 2009)
Sinorhizobium fredii HH103 cgs Mutants	Cyclic-β-glucans	L-, R-TOF/TOF (DHB)	Mutants are unable to nodulate determinate- and indeterminate nodule-forming legumes and overproduce an altered EPS	(Crespo-Rivas et al., 2009)

TABLE 7. (*Continued*)

Shinorhizobium meliloti	Cyclosophoraose or succinoglycan monomer	MALDI	Used for the synthesis of selenium nanowires	(Lee et al., 2009j)
Streptococcus equi	Hyaluronic acid	Ovine testicular hyaluronidase type V, TOF	FACE assay. MALDI to characterize 2-AA glycans	(Kooy et al., 2009)
Upis ceramboides (Alaskan beetle)	Xylomannan	*endo*-β-(1→4)-xylanase, TOF/TOF (DHB)	First identification of a non-protein anti-freeze compound	(Walters et al., 2010)
Commercial	Chitosan oligosaccharides	Endo-β-1,4-GlcNAc-ase, TOF/TOF (DHB)	Analysis of commercial samples and preparation of sample with $GlcNAc_{5\text{-}12}$	(Chen et al., 2010b)
Not stated but has been found in *Cryptococcus neoformans*	Chitosan	TOF	Human macrophage activation shown to be triggered by chitotriosidase-mediated chitin and chitosan degradation	(Gorzelanny et al., 2010)

[1]Format (not all items present): MALDI method (matrix), compounds run (derivative), other methods.

LoCascio et al. (2009) have published a method for measuring the consumption of human milk oligosaccharides by 12 strains of *Bifidobacteria*. Oligosaccharides were quantified with deuterated and reduced oligosaccharide standards that were added after bacterial growth and results were processed with in-house software called Glycolyzer after removal of contributions from ^{13}C isotopes. High growth was found for *Bifidobacterium longum* biovar *infantis* strains, which consumed nearly all available substrates, while other bifidobacterial strains showed low or only moderate growth ability.

Other examples of the use of MALDI analysis of milk glycans are listed in Table 8.

E. Glycoproteins

Glycoproteins and their attached *N*- and *O*-glycans is possibly the largest group of compounds that have been analyzed by MALDI, catalyzed largely by developments in the biotechnology industry. Analysis of these compounds has been reviewed by many authors (Table 9). *N*-glycans are normally attached to an asparagine residue in a Asn-(Xxx)Ser-(Thr) consensus sequence where Xxx is any amino acid (Xxx) except proline However, Asn-linked *N*-glycans have recently been found at the 0.5–2.0% level on a non-consensus amino acid sequence (TVSWN[162] SGAL) in the C_H1 domain of human antibodies and on IgG1 (Valliere-Douglass et al., 2009b).

1. Isolation and Concentration of Glycoproteins and Glycopeptides

Many investigators have published methods for glycoprotein enrichment. Solid-phase glycan/glycoprotein capturing methods have become popular in recent years and some of these have been highlighted in an article by Zhang, Lu, and Yang (2010g).

TABLE 8. Use of MALDI-MS for the Characterization of Carbohydrates From Milk and Milk Products

Source	Methods[1]	Notes	Reference
Camelus bactrianus (Bactrian camel)	R-TOF (DHB)	Structural determination	(Fukuda et al., 2010a)
Human milk oligosaccharides	FT-ICR (DHB)	Study of the ability of 16 gut-related bacteria to grow on milk oligosaccharides	(Marcobal et al., 2010)
Human milk fat globules	FT-ICR (DHB)	Structural determination of gangliosides	(Argov-Argaman et al., 2010)
Human and cow	MALDI	Gastrointestinal uptake and immunology	(Eiwegger et al., 2010)
Seal (bearded and hooded) milk	TOF, QIT-TOF (DHB), glycans (2-AB)	Structural determination	(Kinoshita et al., 2009)
Whey permeate from Gorgonzola cheese	FT-ICR (DHB), glycans	14 Compounds. Half in common with human milk	(Barile et al., 2009)

[1]Format (not all items present): MALDI method (matrix), other methods, compounds analysed.

TABLE 9. Reviews and General Articles on the Analysis of Glycoproteins

Subject	Comments	Citations	Reference
Determination of glycosylation sites and site-specific heterogeneity in glycoproteins	Short review with comments on specific papers	47	(An et al., 2009a)
Historical overview of glycoanalysis	Summarizes historical methods and recent trends	127	(Bielik & Zaia, 2010)
Strategies for analysis of the glycosylation of proteins: Current status and future perspectives	Glycan structure, lectins, glycan release, HPLC, exoglycosidase digestion, CE, HPAEC, NMR, MS	119	(Brooks, 2009)
Analytical progress for protein glycosylation in China	Glycoproteins, glycopeptide enrichment, lectin arrays and MS	41	(Cao et al., 2009)
Glycosite analysis in glycoproteomics by mass spectrometry	*N*- and *O*-glycosylation and *O*-GlcNAc-ation	-	(Chen et al., 2010c)
Identification and quantification of protein posttranslational modifications	Phosphorylation, glycosylation, ubiquitination and sumoylation	183	(Farley & Link, 2009)
Mass spectrometric methods for analysis of glycosylation modifications in bacterial pathogens	General methods for *N*- and *O*-linked glycan analysis. Concentrates on hyman pathogens	218	(Graham & Hess, 2010)
Analytical characterization of monoclonal antibodies	Small section on MALDI-TOF analysis	49	(Harris et al., 2010b)
Structure analysis of *N*-glycoproteins	Mass spectrometric methods for *N*-linked glycan analysis	21	(Henning et al., 2009)
Characterization of antibody glycans	Practical details of several methods including MALDI	44	(Janin-Bussat, et al., 2010a)
Characterization of antibody glycans by mass spectrometry	Practical details of mass spectral methods	47	(Janin-Bussat, et al., 2010b)
Recognition of endogenous ligands by C-type lectins	Mainly summary of authors' work. MALDI analysis of *N*-glycans	46	(Kawasaki & Kawasaki, 2010)
Mass spectrometry of sulfated *N*- and *O*-glycans	Methods for permethylation and interpretation of negative ion MS/MS spectra	32	(Khoo & Yu, 2010)
Development of structural elucidation of *N*-glycans	Historical development; many techniques (little MALDI)	92	(Lee, 2009)
Glycosylation of milk proteins	(In Japanese)	32	(Li et al., 2010d)
Analysis of protein post-translational modifications by MS	-	50	(Marczak & Novotny 2009b)
General review of methods for glycoprotein analysis	Glycan release, HPLC, mass spectrometry, NMR	93	(Mariño et al., 2010)
High-sensitivity analytical approaches to the analysis of *N*-glycans	General review	87	(Mechref & Novotny 2009b)
Glycomic analysis by CE-MS	Short section on interfaces with MALDI MS	97	(Mechref & Novotny, 2009a)
Analysis of glycosylation and other post-translational modifications by MS	Recent mass spectrometric methods.	322	(Morelle, 2009)
Mass spectrometry in the analysis of *N*-linked and *O*-linked glycans	Mainly applications	50	(North et al., 2009)
"Glycomics: Methods and Protocols". Methods in Molecular Biology, Vol 534	Several reviews and methods	-	(Packer & Karlsson, 2009)
Review MS-based targeted protein (and glycoprotein) quantification	Use of stable isotopes, mainly proteins, few glycoproteins..	111	(Pan et al., 2009)
Protein glycosylation analysis with capillary-based electromigrative separation techniques	Little MALDI. Large tables of applications	195	(Pattky & Huhn, 2010)

TABLE 9. (*Continued*)

Analysis of erythropoietin and analogs	Survey EPO and of several analytical methods including MALDI, chromatography	175	(Reichel & Gmeiner, 2010)
Application of proteomics in biomarker discovery	Mainly proteins and glycoproteins. Table of recent applications	139	(Tambor et al., 2010)
Glycoproteomics: Past, present and future	Short historical review	46	(Tissot et al., 2009)
Glycome profiling using modern glycomics technology: technical aspects and applications	Review of glycan profiling methods over last five years	90	(Vanderschaeghe et al., 2010)
Comparative glycoproteomics: approaches and applications	Lectins and MS with applications to cancer and neurology	58	(Wei & Li, 2009)
Structural glycomics using hydrophilic interaction chromatography with MS	ESI and MALDI analysis	78	(Wuhrer et al., 2009a)
Modification-specific proteomics in plant biology	Small section on glycoproteins	127	(Ytterberg & Jensen, 2010)
Mass spectrometry and glycomics	General review	223	(Zaia, 2010)
Use of nanoparticle-enrichment methods for glycoproteins and glycopeptides	Use for enrichment of low abundance and post-translationally modified peptides	101	(Zhang et al., 2010f)
Analysis of protein glycosylation and phosphorylation using liquid phase separation, protein microarray technology, and mass spectrometry	Protocol based on lectin affinity enrichment for glycoproteins	39	(Zhao et al., 2009a)

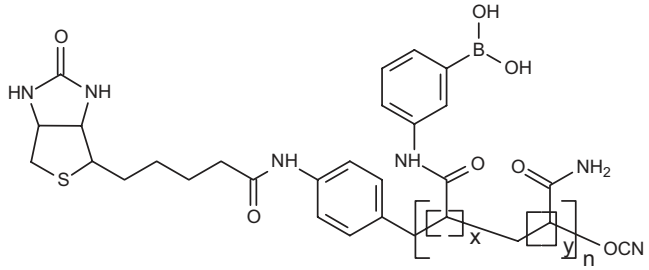
Enrichment strategies for glycopeptides based on lectin-affinity chromatography and polysaccharide hydrophilic affinity physicochemical chromatography have been discussed by Ito, Hayama, and Hirabayashi (2009b). The combined use of these techniques effectively removes non-glycosylated peptides.

a. Use of boronic acids

The ability of boronic acids to form cyclic derivatives with the *cis*-dihydroxy groups present in most glycans has been extensively used. Thus, 3-aminophenylboronic (APB) acid (**5/42**)-functionalized beads, mesoporous silica, and nanodiamonds have been developed to enrich glycosylated peptides and proteins but the direct immobilization of the APB group was found to be insufficient to suppress nonspecific adsorption/adhesion. Consequently Jang et al. (2009b) have designed a self-assembled monolayer (SAM)-based plate, which contained a spacer group such as oligo(ethylene glycol) to reduce the nonspecific adsorption/adhesion, for direct detection of glycoproteins after affinity-capture (or enrichment) on the plate. The utility of the plate was demonstrated with model glycoproteins such as ribonuclease G and TF.

A two-stage glycopeptide enrichment technique using boronate-functionalized beads has been developed by Chen et al. (2010f). Samples were incubated with the functionalized magnetic beads in slightly alkaline conditions at room temperature for about 1 hr with gentle shaking. The beads were washed and the enriched glycoproteins/peptides were eluted under acid conditions and dried in a Speed-Vac evaporator. The glycoproteins were then either dissolved in 50 mM ammonium bicarbonate and digested by Lys-C overnight or separated by sodium dodecyl sulfate (SDS)–polyacrylamide gel electrophoresis (PAGE) and the resulting gel-bands were digested in-gel by Lys-C overnight. The compounds were then ready for a second enrichment. Alternatively, digestions could be carried out with trypsin. Analysis was by MALDI-TOF.

Boronic acid functionalized nanoparticles have also been used to concentrate antibodies by capturing the carbohydrates attached to the Fc region of IgG (Lin et al., 2009b). Chalagalla and Sun (2010) have prepared a boronic acid-containing polymer capped with biotin (**57**) for linkage to a magnetic bead and used the product for glycan capture and Lin et al. (2010f) have constructed magnetic nanoparticles with immobilized APB acid for glycoprotein capture. "SnO_2@Poly(HEMA-co-St-co-VPBA)" Core-shell nanoparticles containing boronic acid groups have been prepared by of copolymerization between 2-hydroxyethyl methacrylate grafted (**58**) on SnO_2 nanoparticles, styrene, and 4-vinylphenylboronic acid (VPBA, **59**). They have been used to extract tryptic peptides from HRP, bovine asiloTF and human serum glycoproteins. Analysis was by MALDI-MS/MS using an AXIMA QIT instrument (Sheng, Xia, & Yan, 2010).



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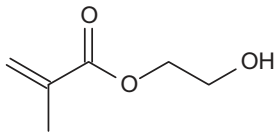
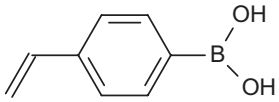


2-Hydroxyethyl methacrylate, **58**



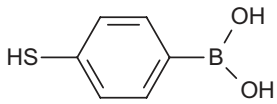
4-Vinylphenylboronic acid, **59**

A novel boronic acid functionalized mesoporous silica, which holds the attractive features of high surface area and large porosity has also been used to concentrate glycopeptides. In comparison to direct (traditional) analysis, this method was stated to enabled two orders of magnitude improvement in the detection limit of glycopeptides irrespective of the nature of the attached glycans (Xu et al., 2009). The same group (Zhang et al., 2009d) has also synthesized boronic acid functionalized core-satellite composite nanoparticles that possess both the superparamagnetic properties of magnetic nanoparticles and the surface chemistry of AuNPs. Glycoproteins or glycopeptides could be obtained in high yield by use of a magnet. The composite nanoparticles were used to enrich glycosylated proteins from human colorectal cancer tissues for identification of *N*-glycosylation sites. In all, 194 unique glycosylation sites mapped to 155 different glycoproteins were identified, of which 165 sites (85.1%) were new.

Boronic acid functionalized gold-coated Si wafers have been used as MALDI plates to isolate and enrich glycopeptides (Xu et al., 2010b). This method was claimed to be beneficial for several reasons. Thus, solution transfer and eluting steps required in conventional enrichment strategies were not needed, thereby reducing sample loss. Secondly, the lower limits of detection of glycopeptides were said to have been increased by two orders of magnitude. Thirdly, non-specific bindings were not detected even when non-glycopeptides were 100 times more concentrated than glycopeptides. Furthermore, glycopeptides could be detected in the presence of 200 mM ammonium bicarbonate or the physiological buffer, PBS.

In a related method (Tang et al., 2009a; Yao et al., 2009), AuNPs were first spotted and sintered onto a stainless steel plate, then modified with 4-mercaptophenylboronic acid (**60**) to provide a porous substrate with a large surface for capturing glycopeptides from peptide mixtures. The captured peptides were then analyzed by MALDI-TOF MS simply by deposition of a DHB matrix. The technique enabled sample enrichment, washing and detection steps to be fulfilled on a single MALDI target plate. Well-characterized glycoproteins, such as HRP and asialofetuin, were employed as standards to investigate the enrichment efficiency. Fe_3O_4@C@Au magnetic microspheres functionalized with 4-mercaptophenylboronic acid have been synthesized by the same group (Qi et al., 2010) and successfully used for enrichment of glycoproteins and glycopeptides.

A polyfunctional device has been constructed from *Macroporous silica* foam (MOSF) containing boronic acid (BMOSF) or amino groups (NH_2-MOSF) and used to immobilize enzymes



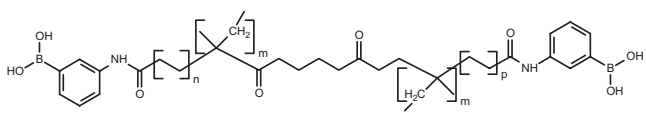
4-Mercaptophenylboronic acid, **60**

such as trypsin and selectively enrich glycopeptides. Use of the device considerably speeded up hydrolysis times as demonstrated with glycopeptides from HRP (Qian et al., 2010).

Tang et al. (2010a) have immobilized the lectin Con A on APB acid-functionalized magnetic nanoparticles using methyl α-D-mannopyranoside as a linker. The selective capturing ability of the Con A-modified nanoparticles was tested using standard glycoproteins and cell lysate of human hepatocelluar carcinoma cell line 7,703. Regeneration of the protein-immobilized nanoparticles could easily be performed by utilizing the reversible binding between the boronic acid and the sugar. ConA has also been used in conjunction with hollow fiber flow field-flow fractionation (HF5) to preconcentrate high mannose type *N*-linked glycoproteins from bacterial lysates as exemplified by glycoproteins from *Streptococcus pyogenes* (Kang et al., 2010). The specificity of *Datura stramonium* agglutinin (DSA) for tri- and tetra-antennary glycans has been utilized to enrich human liver glycoproteins containing these larger glycans which were then separated and identified by SDS–PAGE followed by MALDI-TOF analysis (Sun et al., 2009b).

The performance of chromatographic columns consisting of agarose-bead-bound 3-aminophenyl boronic acid, agarose-bound wheat-germ agglutinin (WGA) or a mixture of both compounds (boronic acid lectin affinity chromatography, BLAC) has been evaluated for glycoprotein enrichment using the model proteins of RNaseB and trypsin inhibitor in the presence of the non-glycosylated proteins, myoglobin (neutral) and lysozyme (basic) over a wide temperature range (5–65˚C). The results showed that glycoaffinity micropartitioning at 25˚C provided the highest recovery rate for glycoprotein enrichment. A large amount of lysozyme was present in the elution fractions of the 3-aminophenyl boronic acid-containing micropartitioning columns due to an ion-exchange mechanism occurring between the positively charged protein and the negatively charged stationary phase. At 65˚C, nonspecific interactions with the agarose carrier prevailed, evidenced by the presence of myoglobin in the eluate (Olajos et al., 2010).

A novel boronate affinity monolith, poly-(3-acrylamidophenylboronic acid-co-ethylene dimethacrylate) (**61**) has been prepared in 530 mm capillaries by a one-step *in situ* polymerization procedure (Chen et al., 2009b). The monolith was used to separate glycopeptides from peptides produced from HRP and to separate this glycosylated protein from non-glycosylated bovine serum albumin (BSA). The MALDI-TOF spectrum of the HRP peptides showed little evidence of the presence of glycopeptides before passage through the capillary but revealed abundant glycopeptide ions after treatment.



61

b. Other solid-phase methods

Titanium dioxide (TiO_2) microspheres, synthesized by a sol–gel method, have a high affinity for the acid groups of sialic acids and peptides. They have successfully been used for simultaneous enrichment of glycopeptides and phosphopeptides from, for example bovine RNaseB and human IgG (Yan et al., 2010). Detection was by ESI but the method would be equally applicable to MALDI-TOF analysis.

Mysling et al. (2010) have used ZIC-HILIC in a microcolumn format for SPE and glycoprotein enrichment involving trifluoroacetic acid (TFA) ion pairing to increase the hydrophilicity difference between glycopeptides and non-glycosylated peptides. Three mobile phases were investigated: 2% formic acid, 0.1% TFA and 1% TFA all containing 80% acetonitrile and experiments were conducted on single glycoproteins, a five-glycoprotein mixture and depleted plasma. The presence of TFA, particularly at the 1% level, in the mobile phase significantly improved the glycopeptide enrichment (3.7-fold) as evaluated by MALDI-TOF MS and RP-LC-ESI-MS/MS.

Four types of hydrazine functionalized carboxyl and epoxysilanized magnetic particles (HFMP) have been developed by Sun et al. (2010a) for isolation of glycopeptides. Particles prepared by adipic dihydrazide functionalization from carboxylsilanized magnetic particles yielded the maximum capture capacity. The method was verified by successful isolation of all formerly glycosylated peptides from standard glycoproteins (fetuin, RNaseB, and human serum albumin (HSA)) and by identification of their glycosylation sites.

c. Other techniques

MALDI-TOF MS has been used by Carvalho et al. (2009) to characterize the α- and β-subunit of recombinant and pituitary glycoprotein hormones that have been separated by a new method of incubating the glycoproteins overnight with acetic acid (0.5–3.0 M) at 37°C.

2. N-Glycans

a. Use of mass spectrometry to detect glycosylation of proteins

A simple method to detect glycosylation is to measure the mass of a glycoprotein and then to repeat the measurement after incubation with PNGase F to remove the *N*-glycans. The method has been used to detect the presence of *N*-glycans in recombinant bovine CD38 expressed in *Pichia pastoris* (Muller-Steffner et al., 2010). The molar masses of non-glycosylated (29,343 Da) and penta-glycosylated *Thermomyces lanuginosus* lipase (40,906) as measured by MALDI-TOF MS have confirmed glycosylation and shown that each glycan-moiety adds approximately 2,000 Da to the molar masses (Pinholt et al., 2010). In another example, Cu/Zn superoxide dismutase monomer was determined to have a mass of 17,097 Da before deglycosylation and 15,871 Da afterwards giving a mass for the glycan of about 1,200 (Nedeva et al., 2009).

The difference between the sequence mass (33,768 Da) and measured mass of about 44,604 Da of the peroxidase from royal palm tree (*Roystonea regia*) together with the fact that the amino-acid sequence includes 12 possible *N*-glycosylation sites, suggests heavy glycosylation. Glycosylation sites were identified, in this case, by *N*-terminal sequencing and MALDI-TOF-MS analysis of tryptic peptides (Watanabe et al., 2010).

b. Mass spectrometric detection of glycoforms of intact glycoproteins

Although resolution of glycoforms by MALDI-TOF MS is generally inferior to that obtained by ESI, glycoproteins with masses in the region of 60 kDa, containing only a limited number of glycoforms have been resolved successfully as illustrated by the resolution of four glycoforms of antithrombin in a study of altered glycosylation causing antithrombin deficiency (Martínez-Martínez et al., 2010). Glycans appeared to be sialylated biantennary (residue mass 2,204 Da).

Ogawa et al. (2009) have observed resolution of glycoforms of *Stereum purpureum* endopolygalacturonase I produced in *P. pastoris* (36.5 kDa). Three main ion peaks corresponding to the protein with the high-mannose glycans $Man_{8-10}GlcNAc_2$ together with some minor unresolved ions were observed.

c. Detection of glycosylation sites and site occupancy

The most common method for detecting site occupancy is to utilize the conversion of the Asn to which the *N*-glycans are attached to aspartic acid (Asp) when the glycans are released with PNGase F. The increase by one mass unit is readily detected by MS. The method has been used, for example to confirm occupancy of six of the seven potential *N*-linked glycosylation sites in the envelope glycoprotein gp116 and three of the four potential sites in the gp64 protein of the yellow head virus from the *Penaeus monodon* shrimp (Soowannayan et al., 2010).

Periodate oxidation and hydrazide capture on a solid support have been used by Lewandrowski and Sickmann (2009) to study glycosylation sites in human platelet proteins. The bound glycoproteins were sufficiently stable to allow washing, following which the proteins were hydrolyzed. Glycopeptides remained bound to the solid support through the glycan moiety from where they were released with PNGase F and the glycosylation site was identified by means of the Asn to Asp conversion.

A new method using tandem ^{18}O stable isotope labeling (TOSIL) to quantify the *N*-glycosylation site occupancy has been reported (Liu et al., 2010k). Glycoproteins were digested with trypsin and PNGase F in the presence of either $H_2{}^{18}O$ or $H_2{}^{16}O$. Three ^{18}O atoms were introduced into *N*-glycosylated peptides, two at the carboxyl terminus of all peptides and the third at the *N*-glycosylation site. The samples were mixed to give pairs of ions in the resulting MALDI or ESI spectra. A unique mass shift of 6 Da was produced by *N*-glycosylated peptide with a single glycosylation site, whereas non-glycosylated peptides produced an ion pair spaced by only 4 Da. Intensity ratios could be used to monitor site occupancy in various physiological and disease conditions. The method yielded good linearity within a 10-fold dynamic range with the correlation coefficient $r^2 > 0.99$. The standard deviation (SD) ranged from 0.06 to 0.21, for four glycopeptides from two model glycoproteins. The method was used to monitor glycoproteins in the sera from a patient with ovarian cancer and healthy individuals. Eighty-six *N*-glycosylation sites were quantified and *N*-glycosylation levels of 56 glycopeptides showed significant changes. A similar ^{18}O-labeling technique was used by Alvarez-Manilla (2010b) to identify *N*-glycosylation sites in Con-A-extracted glycopeptides from pluripotent murine embryonic stem cells. Glycopeptides rather than glycoproteins were extracted from tryptic digests to avoid false positives produced

from non-glycosylated proteins that were bound to extracted glycoproteins if no digestion had been performed.

Segu et al. (2010b) have published a method for detecting sites occupied by glycans carrying a fucose residue attached to the core. The method made use of the endoglycosidase M which, like PNGase F has a broad spectrum of activity with the exceptions that (a) it is not active on core-fucosylated glycans and (b) it shows reduced activity with larger glycans. The second exception was overcome by conducting incubations in the presence of sialidase, β-galactosidase and β-*N*-acetylhexosaminidase, which reduced the size of the glycans. Then, the results were compared with the products of digestions performed with PNGase F allowing the core-fucosylated sites to be determined. Analyses were by LC/MS but the technique would be equally applicable to MALDI-TOF analysis.

d. Analysis of glycopeptides

Because many glycoproteins are too large and heavily glycosylated for direct analysis by MS, much work is performed on derived glycopeptides, most commonly tryptic glycopeptides. Tryptic cleavage of glycoproteins is frequently hindered by steric hindrance imposed by the glycans but improvements can be made by the use of heat to increase the rate of proteolysis. Segu, Hammad, and Mechref (2010a) have used microwave-assisted enzymatic digestion to achieve higher sequence coverage of several model glycoproteins such as fetuin, TF, and fibrinogen. Efficient digestion was achieved in 15 min at an optimum temperature of 45˚C; there was no apparent loss or partial cleavage of the glycans.

Signals from glycopeptides are often weak or absent from the spectra of mixed peptides and glycopeptides, a situation that can be improved by fractionation of the two compound classes. Wohlgemuth et al. (2009) have investigated several techniques and have shown that hydrophilic interaction chromatography (HILIC) chromatography with ZIC-HILIC and TSKgel Amide-80 are very specific at capturing glycopeptides from mixtures. Sialylated glycopeptides could also be enriched with TiO_2. Capture using a hydrazide column resulted in lower recovery and involved a more complex enrichment scheme. A new material for glycopeptide concentration, termed "click maltose," has been synthesized by linking the alkynyl-derivatized maltose chain to the azide derivatized silica gel through click chemistry. Unlike the rigid structure of Sepharose, the saccharide chain of click maltose exhibits a certain amount of flexibility, which provides a sufficient number of hydroxyl groups for the effective formation of hydrogen bonds with the glycans attached to glycopeptides. The material was used to isolate glycopeptides from IgG, RNaseB, and AGP (Yu et al., 2009a). Cellulose columns have also been used for concentration of glycopeptides (Snovida et al., 2010).

A method for detecting core-fucosylated (CF) glycoproteins for screening purposes has been reported by Jia et al. (2009). After IgG depletion, fucosylated plasma proteins were enriched by use of *Lens culinaris* lectin and the bound glycoproteins were digested by trypsin. These compounds were enriched by use of a 3,000 Da cut-off filter, a procedure that also combines de-salting and concentration. The recovered glycopeptides were then treated with endoglycosidase F3, which specifically cleaves the glycosidic bond between the two proximal (core) GlcNAc residues and leaves the fucosyl-GlcNAc residues attached to the peptides. Four standard glycoproteins, apo-TF, fetuin, rhEPO, and RNaseB, was used to illustrate the method. In addition, a part of the untreated tryptic peptides was treated with PNGase F in order to locate the glycosylation site by the Asn to Asp conversion. Products were detected by MALDI-TOF. In a related method using an ion trap, a neutral loss scan for fucose (146 Da) was also used to detect fucosylation. The methods were applied to the detection of fucosylated glycoproteins in the plasma of healthy subjects and subjects with hepatocellular carcinoma. Over 100 fucosylated glycoproteins and attachment sites were identified, and over 10,000 mass spectra of CF glycopeptide were analyzed.

A method termed the Sulfate Emerging method has been described for specifically extracting sulfated glycopeptides (Toyoda, Narimatsu, & Kameyama, 2009) from mixtures. The method overcomes the often negative contribution from other charged groups in the molecules. To accentuate the negative charge on the sulfate group, basic amino acids were eliminated and carboxylic acids were neutralized as follows: The protein was first hydrolyzed with trypsin and then the positively charged C-terminal lysines (Lyss) and arginines (Args) were eliminated by incubation with carboxypeptidase B. The negative charges of the carboxylic acid groups on the peptides were then neutralized by chemical modification with acetohydrazide using the recently reported quantitative modification of carboxyl groups in sialic acid using this reagent and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (**43**). The sulfated glycopeptides in the mixture were then captured by anion exchange resin with a basic buffer (pH 8.6) in which protonation of histidine residues was suppressed. Finally, the sulfated glycopeptides were eluted from the anion exchange resin by increasing the ionic strength of the elution buffer for analysis by MS.

Rather than trypsin, pronase has been used as a non-selective enzyme to reduce the protein to a single amino acid (Asn) or short peptide attached to *N*-glycans. These compounds are generally smaller than those obtained from *O*-linked glycopeptides, probably because *O*-glycans lie closer to the peptide backbone than *N*-glycans and protect the polypeptide from enzymatic digestion. *N*-Glycans usually rise above the peptide backbone exposing the polypeptide to enzymatic digestion. Dodds et al. (2009) have described immobilized pronase which retains its activity after repeated use for at least 6 weeks.

Use of negative ion detection has been reported by Nwosu et al. (2010) as providing distinct advantages over detection in positive ion mode for the detection of glycopeptides produced by pronase digestion. Analysis in positive ion mode, although most commonly used for glycopeptide characterization, is hampered by potential charge-induced fragmentation of the glycopeptides and poor detection of the glycopeptides carrying sialic acids. Furthermore, CID spectra of glycopeptides in the positive ion mode predominantly yields glycan fragments with minimal information on the peptide moiety. In the study by Nwosu et al., which employed bovine lactoferrin for detection of *N*-glycosylation and κ-casein for *O*-glycosylation, 44 potential *N*-linked glycopeptides were detected in the positive ion mode whereas 61 potential *N*-linked glycopeptides were detected in negative ion mode. Analysis of κ-casein, which contained mainly sialylated glycans, yielded improved results in negative mode.

Experimental details for peptide mass fingerprinting and identification of glycosylation sites have been published by Wilson, Simpson, and Cooper-Liddell (2009).

Unlike the case with released glycans, where a relatively low mass accuracy measurement is usually sufficient to determine the composition in terms of the constituent monosaccharides, the situation is very different for measurements of glycopeptides. Desaire and Hua (2009) have examined the accuracy required and have concluded that in only a few cases can the mass accuracy provided by most commercial instruments be sufficient to unambiguously assign compositions to all glycopeptides in a mixture.

e. N-Glycan release

Once glycosylation sites have been determined, detailed structural analysis of the attached glycans is more conveniently carried out after releasing the glycans from the protein or peptide. Both chemical and enzymatic methods are available but although, in the past, chemical release with hydrazine was popular, most investigators now prefer enzymatic methods.

i. Enzymatic release

PNGase F. Peptide *N*-glycosidase F (PNGase F), an amidase, is the most popular enzyme for cleaving *N*-glycans from their Asn linkage site. It shows a broad range of substrate specificity with the exception that it does not release glycans bearing a fucose residue attached to position 3 of the reducing-terminal GlcNAc; in these cases, PNGase A is appropriate. PNGase F cleaves the entire glycans, which are released as the corresponding glycosylamines. These compounds rapidly hydrolyze to the glycan with retention of the reducing terminus. This method is, thus, distinctly advantageous to techniques such as β-elimination, popular with *O*-glycans (see below) because this site can conveniently be used to attached tags for fluorescence or other detection methods. Wang et al. (2009i) have recently found that the activity of the enzyme towards denatured glycoproteins can be enhanced by removal of the *N*-terminal H1 helix from the enzyme.

Bereman et al. (2009b) have studied methods for optimizing the release of glycans with this enzyme. Dialysis of plasma prior to incubation was found to have little or no effect. However, microwave-assisted glycan release was found to be beneficial; 20 min at 20˚C with approximately 250 W was found to give optimal results. Surprisingly, no protease digestion was required as needed with standard incubation methods, and it was found that an 18-hr incubation with no detergent (NP40) led to the greatest ion abundance of glycans from plasma glycoproteins. Data could be obtained in less than 1 day from raw plasma samples utilizing microwave irradiation. PNGase F-glycan release from human serum glycoproteins has been achieved in 10 min by using a constant microwave power of 20 W, giving a temperature of 44˚C (Kronewitter et al., 2010). In this study, the glycans were recovered by SPE using a robotic liquid handler and examined by MALDI with an FT-ICR instrument from DHB. Replicate analysis gave coefficients of variation of less than 0.2.

The standard protocol for *N*-glycan release from glycoproteins requires relatively long deglycosylation times (from several hours to, usually, overnight) and relatively high enzyme concentration (from 1:250 to 1:500 enzyme/substrate ratio). Szabo, Guttman, and Karger (2010a) have used a high-pressure method, both to reduce the reaction time and the amount of enzyme required. Thus, a pressure-cycling device was use to cycle the pressure from atmospheric to as high as 30 kpsi. Greater than 95% release of the Asn-linked glycans from bovine RNaseB, human TF, and polyclonal human immunoglobulin was achieved in only a few minutes using as low as 1:2,500 enzyme: substrate molar ratio.

A reactor with immobilized PNGase F on a monolithic polymer support in a capillary has been developed that allows fast and efficient release of *N*-linked glycans. Performance was determined with RNaseB, chicken ovalbumin, and human IgG with detection by MALDI-TOF MS. The optimized reactor was integrated into a multidimensional system comprising on-line glycan release and hydrophilic interaction liquid chromatography (LC) followed by ESI-TOF MS detection. Using this system, human IgG was deglycosylated at room temperature in 5.5 min to an extent similar to that achieved with the soluble enzyme after 24 hr at 37˚C (Krenkova, Lacher, & Svec, 2009).

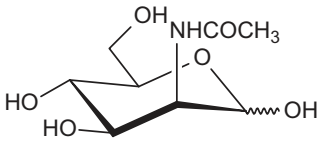
Immobilization of PNGase F on detonation nanodiamonds has resulted in glycan release from glycoproteins in less than 10 min (Wei et al., 2010). The method, using trypsin immobilization, also gave good results and proved to be better for proteolysis than the use of commercial immobilized trypsin beads.

Artefacts associated with PNGase release of *N*-glycans. For solution release of glycans, the glycoprotein is usually denatured by reduction and alkylation or by use of detergents or other compounds such as urea. In general, low concentrations of urea (<3 M) do not usually cause irreversible protein denaturation. Indeed, PNGaseF itself is stable in 2.5 M urea at 37˚C for 24 hr and still possesses about 40% activity in 5 M urea. However, other glycoproteins appear more susceptible. For example, analysis by SDS–PAGE and MALDI-TOF MS have revealed that additional 2.5 kDa of glycans can be released by PNGase F if the deglycosylation is conducted in 2 M urea suggesting that urea treatment exposes a glycosylation site that was previously inaccessible to PNGaseF (Lee et al., 2009g). Use of urea, however, can cause problems with the released glycans because it has been reported to compete with water for hydrolysis of the initially formed glycosylamines with the formation of a urea complex (Omtvedt et al., 2004).

Another artefact that has been found in glycans released with PNGase F involves the reaction of the glycosylamines with H_2S to form the glycan-SH analogue. The H_2S arises from dithiothreitol (DTT, **6/44**), a reagent used for protein alkylation and present in some commercial preparations of the reagent. The consequence of this reaction is an increase in 16 Da giving the impression, from a simple mass measurement, that the glycan has an additional oxygen atom. Addition of 16 Da can also be observed in MALDI spectra as a consequence of the formation of $[M+K]^+$ rather than $[M+Na]^+$ ions, but this possibility can be excluded by formation of $[M+Cs]^+$ ions whereupon the 16 Da mass increase will still be present. The reaction with H_2S was first noted with glycans from human IgG and negative ion MS/MS of the artefactual products located the 16 Da to the reducing-terminal GlcNAc residue. The negative ion fragmentation pattern was the same as that expected for a glycan with a hexose attached to the 6-position of the residue rather than fucose (deoxy-Hex) that was actually the case. This result emphasizes how careful one must be, not only in deducing compositions from glycan masses but also in interpreting their MS/MS spectra (Harvey & Rudd, 2010).

Another artefact of the PNGase F release step, detectable by CE but not by MS has been identified as the product of epimerization of the terminal GlcNAc residue to *N*-

acetylmannosamine (ManNAc, **62**) under the slightly basic conditions usually employed in the release reaction. Reducing the pH to 5.5 effectively removed the by-product (Liu, Salas-Solano, & Gennaro, 2009h).



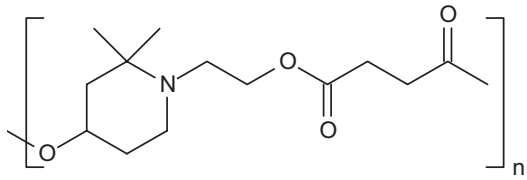
N-Acetylmannosamine (ManNAc), **62**

Other endoglycosidases. Another popular enzyme for *N*-glycan release is endo H which cleaves the chitobiose core of high-mannose and hybrid glycans but not complex ones, leaving a GlcNAc residue, with any linked fucose, attached to the protein. Pace et al. (2009) have made use of this property to release and identify minor glycans in IgG without interference from the more abundant complex glycans. Endo F1 has a similar specificity and has been used by, for example, Voutilainen et al. (2010) to detect glycosylation in *Talaromyces emersonii* cellobiohydrolase Cel7A produced in the yeast *Saccharomyces cerevisiae*.

Ammonium hydroxide/carbonate-based chemical deglycosylation and PNGase A enzymatic release have been compared for glycan release from a plantibody produced in tobacco plants (Triguero et al., 2010). Although both methods gave similar profiles as evaluated by HPLC of 2-AB derivatives, the main drawback of the chemical release method was that it induced degradation of α1,3-fucosylated *N*-glycans.

ii. Extraction and purification of released glycans. Clean-up of samples prior to MS is crucial to obtaining good spectra. Many methods are in use; porous graphatized carbon (Buser et al., 2010) is popular and we have found Nafion membranes (Börnsen, Mohr, & Widmer, 1995) to be convenient at removing both salts and some hydrophobic compounds. Avoiding the introduction of contaminants is also important. Disposable plasticware such as plastic test tubes that are normally used to process samples have been shown to be a major source of contamination. The contaminants, which produce ions, mainly prompt fragments across the entire mass range to about *m/z* 3,000, originate from polymers that are used to protect the plastic against oxygen or UV light degradation. Such compounds are hindered amine light stabilizers (HALSs) used in modern polyolefin (polypropylene, polyethylene) stabilization. The polymeric agent: poly-(*N*-β-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidinyl succinate, **63**), known as Tinuvin-622 or Lowilite 62, has been found to leach from laboratory polypropylene or polyethylene plastic test tubes into solvents used for sample preparation. 1.5 mL plastic tubes were found to be the major source of the contamination but the authors of the paper found that this could be minimized by using large solvent volumes of, for example, matrix solution (Sachon et al., 2010).

Amano and Nishimura (2010) have used two kinds of hydrazide-functionalized glycobeads, termed GlycoBlot H and GlycoBlot ABC of which the latter carries an additional fluorescent probe, to extract PNGase F-released *N*-glycans from solution. Sialic acids were then converted into methyl esters using the 3-methyl-1-*p*-tolyltriazene (MTT, **6/23**) reagent de-



Poly-(*N*-*β*-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidinyl succinate, **63**

scribed by Miura et al. (2007) and the products were examined by MALDI-TOF MS after release of the glycans from the beads by mild acid hydrolysis. The method was used to examine human serum glycoproteins for cancer biomarkers. Full experimental details of the extraction and derivatization procedure are given in the paper. Enrichment of serum and cellular glycoproteins with Glycoblot H beads has also been used for *O*-glycan analysis (Miura et al., 2010b). Glycans were released from human milk osteopontin and urinary MUC1 glycoproteins with ammonium carbamate and the method was proposed as ideal for identification of biomarkers.

A method for sequentially enriching sulfated glycans by strong anion-exchange chromatography according to their degree of sulfation has been described by Lei, Novotny, and Mechref (2010). The method is based on modifying the binding ability of strong anion-exchange material with different sodium acetate concentrations, thus enabling selective binding and a subsequent elution of different glycans according to their degree of sulfation. Before this enrichment, the negative charge on any sialic acid was eliminated by permethylation. The method was initially optimized using sulfated oligosaccharide standards and then used to examine the sulfated *N*-glycans from bTSH, a glycoprotein possessing mono- and disulfated *N*-glycans.

f. Analysis of released glycans

Ahn et al. (2010) have obtained good resolution of *N*-glycans as their 2-AB derivatives using HILIC columns packed with 1.7 μm sorbent. Glycans were released from RNase B with PNGase F and extracted using a microElution HILIC SPE 96-well plate. The labeled glycans were also extracted from the preparative reagents using the same plate and their integrity was checked by MALDI-TOF MS.

In another technique, Guillard et al. (2009) have experimented with optimizing a linear ion trap instrument for automated measurement of permethylated *N*-glycans in serum. Glycans were released with PNGase F, cleaned with graphitized carbon and permethylated with the sodium hydroxide method. DHB, although the favored matrix for carbohydrates, failed to give the necessary reproducibility because of the large crystal size. CHCA, on the other hand, proved to be satisfactory.

Full experimental details for analysis of *O*- and *N*-linked glycans have been published by several authors (Azadi & Heiss, 2009; Morelle et al., 2009a; North et al., 2010b).

g. Total methods for glycoprotein structure

There have been many reports of methods for total glycoprotein analysis of which the following are representative. A small-scale method for *N*-glycan release and analysis from plants used to produce recombinant glycoproteins has been described (Karg et al., 2009). Concentration, protease digestion and deglycosylation are carried out in a single concentrator unit

without the need for intermittent purification. This approach minimized adsorptive losses and facilitated handling. The plant protein was concentrated in a unit with a 5 kDa cutoff and after buffer exchange, pepsin digestion was carried out in the concentrator overnight. Deglycosylation was carried out with PNGase A for 24 hr. Released *N*-glycans were purified using reversed-phase and cation exchange chromatography in micro-columns and analyzed by MALDI-TOF MS without derivatization.

A chip-based reversed-phase LC/MS method for *N*-glycan analysis suitable for biomarker discovery has been developed by Alley et al. (2010). *N*-Glycans were released from bovine fetuin as a model glycoprotein and human serum glycoproteins with PNGase F and reduced to alditols with an ammonia-borane complex. The glycans were then permethylated in dimethylformamide to avoid artefacts in MS measurements and their structures were checked by MALDI-TOF measurements. Reversed-phase microfluidic LC of the permethylated *N*-linked oligosaccharide alditols was then performed and was shown to resolve some closely related structures. Optimized LC gradients, together with nanospray MS were then used with human serum samples to distinguish breast cancer patients from control individuals.

A previously established two-dimensional HPLC technique has been adapted as a HPLC-MALDI MS method for *N*-glycan analysis by Gillmeister et al. (2009). Glycans were released from glycoproteins with PNGase F purified with graphitized carbon and fluorescently labeled with 2-AP. The labeled glycans were analyzed on a 2-mm reversed phase (RP) HPLC column and spotted onto a MALDI-TOF MS plate together with the DHB matrix using an automated plate spotter. The method gave a 100-fold reduction in the required amounts of starting protein compared with the earlier procedure. The entire process could be carried out in 2–3 days for a large number of samples as compared to 1–2 weeks per sample for previous two-dimensional HPLC methods. The modified method was verified by identifying *N*-glycans from an IgG antibody from human sera samples and applied to analysis of tissue plasminogen activator (TPA) from CHO cell cultures under varying culture conditions.

Kim et al. (2009b) have released glycans on a polyvinylidine difluoride (PVDF) membrane with PNGase F and cleaned them with graphitized carbon contained in a 96-well plate before converting them into Girard's T derivatives to introduce a constitutive cationic charge for quantification. Analysis was by MALDI-TOF MS and the robust method was used to profile *N*-glycans from ovarian cancer patients using as little as 5 μL of serum.

A high-throughput method for the analysis of human plasma glycomes using a 48-channel multiplexed capillary gel electrophoresis (CGE) DNA sequencer with laser-induced fluorescence detection (CGE-LIF) system has been described with MALDI-TOF MS used to provide structural information (Ruhaak et al., 2010c). Glycans were released from plasma glycoproteins in a 96-well plate using PNGase F and converted into APTS derivatives with the help of 2-picoline borane (**27**) as the reducing agent. Analysis by CGE-LIF using the DNA sequencer allowed 96 samples to be analyzed in only 2.5 hr (the experimental time was longer because of two overnight incubations). The method was applied to a study of glycosylation patterns during first, second, and third trimesters of pregnancy, as well as 6 weeks, 3 months, and 6 months postpartum.

Although analysis of glycoproteins carrying neutral glycans is now routine, analysis of glycoproteins with sialylated glycans is more difficult. Hao, Ren, and Xie (2010) have approached the problem by first performing a tryptic digestion to give peptides and glycopeptides. Peptide mass fingerprinting was performed on the peptides in order to identify the protein. The glycopeptides, separated by HILIC chromatography, were examined by MALDI-TOF MS and MS/MS and treated with PNGase F to release the glycans, which, together with the resulting peptides were again examined by MS. The Asn to Asp conversion in the peptide fraction enabled the glycosylation site to be identified. Finally, the glycans were desialylated with dilute HCl and again analyzed by MS. The technique was applied to glycoproteins from human serum separated by 2-D electrophoresis and the differences in *N*-glycosylation were successfully determined for α1-antitrypsin between different gel spots.

In another method, sialylated glycoproteins have been selectively periodate-oxidized, captured on hydrazide beads, trypsinized and released by acid hydrolysis of the sialic acid glycosidic bonds. Mass spectrometric fragment analysis allowed identification of glycan structures and additional fragmentation of deglycosylated ions yielded peptide sequence information which allowed glycan attachment sits to be identified together with identification of the protein. Using this method, the investigators identified 36 *N*-linked and 44 *O*-linked glycosylation sites on glycoproteins from human cerebrospinal fluid (Nilsson et al., 2009).

Related to this method is one developed by Klement et al. (2010) for enrichment of *O*-GlcNAc-modified proteins. Glycoproteins were again oxidized with periodate and captured by hydrazide resin capture. Rather than release of the peptide enzymatically, the glycopeptide was released by hydroxylamine treatment which also converted the aldehyde groups of the oxidized glycan to oximes. The open nature of the carbohydrate ring, following oxidation, lead to the production of characteristic fragment ions facilitating both glycopeptide identification and site attachment. The method was applied to analysis of α-crystallin A and the *Drosophila* proteaosome.

h. Comparisons of methods for N-glycan analysis

A comparative study of three techniques, MALDI-TOF, SDS–PAGE and CGE-on-a-chip, for measuring the MWs of large glycoproteins has been reported by Müller et al. (2010b). It was found that all three techniques were capable of determining the MW of all high MW (glyco)proteins tested. The non-commercial CGE-on-a-chip assay allowed electrophoretic separation of proteins in the MW range from 14 kDa to 1 MDa. MW assignment was limited to 500 kDa in the case of SDS–PAGE but with the proper matrix (THAP for most glycoproteins, sinapinic acid for α2-macroglobulin) and sample preparation, analysis with a standard MALDI-TOF-MS provided accurate MWs for all high MW proteins up to 1 MDa.

Three methods for *N*-glycan characterization, namely MALDI-MS of glycopeptides from tryptic digestion, negative-ion ESI-MS/MS of released *N*-glycans, and normal-phase HPLC of fluorescently labeled glycans, in combination with exoglycosidase sequencing, have been evaluated for glycan identification using monoclonal antibodies expressed in tobacco plants as model compounds (Triguero et al., 2010). The MS

methods identified the major glycans, but the HPLC method was found to be the best for identification and relative quantitation. Negative-mode ESI-MS/MS easily provided direct identification of features such as the linkage position of the fucose residue linked to the inner core GlcNAc residue.

Grey et al. (2009) have developed a high-performance ion exchange chromatographic method for *N*-glycan analysis and have shown that it gives very similar results to analysis by MALDI-TOF. A series of standard glycans was examined and the method was extended to the analysis of *N*-glycans released from IgG1.

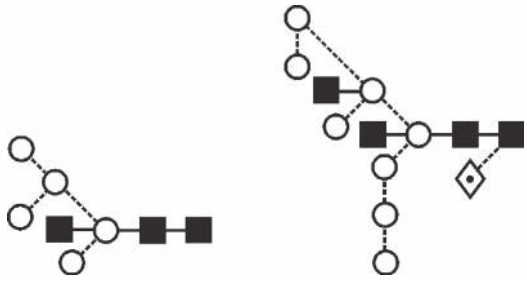
An inter-laboratory study involving eleven UK laboratories using their routine glycan analysis procedures looked at reproducibility on glycan profiling from *N*-glycans released before the study from four glycoproteins, human and bovine AGP, bovine pancreatic RNaseB and human serum immunoglobulin G (hIgG). Data interpretation focused on the relative amounts of different glycan structures present, the degree of sialylation, galactosylation profiles, fucosylation, and bisecting GlcNAc content and the number of glycan components identified. All laboratories found high levels of sialylation for human and bovine AGP, but varying amounts of di-, tri-, and tetra-antennary glycans. Values obtained from mass spectrometric and chromatographic methods clustered separately. The proportion of the major $Man_5GlcNAc_2$ from RNaseB was between 29% and 62%. Proportions of fucosylated and bisected GlcNAc glycans from hIgG were between 58% and 96% and 9% and 23%, respectively. Mass spectrometric approaches consistently identified more glycan species, especially when both *N*-glycoylneuraminic acid (Neu5Gc) and Neu5Ac were present (Thobhani et al., 2009).

A recent test of the ability of several laboratories to identify *N*-glycans released with PNGase F from a mixture of four glycoproteins, asialo-fetuin, chicken ovalbumin and both human and bovine AGP has also yielded some alarming results (Orlando, Leymarie, & Keck, 2010). Although 18 of the 19 laboratories detected the presence of fucosylated complex *N*-glycans, 14 of them incorrectly located the fucose to the core GlcNAc of human AGP rather than to an antenna. All nine of the labs using MS (not MS^2) misidentified the site and all five of laboratories relying on software to identify the site also reported it incorrectly. Although the ionic charge was not specified, it is assumed to be positive because it would be impossible to make this mistake with negative ion fragmentation. Features such as the position of fucose residues produce diagnostic cross-ring fragments whose mass depends on the location of the fucose residue (Harvey et al., 2008). Such mis-identifications are particularly worrying because serum AGP is elevated in inflammatory disease and is of potential use as a biomarker. Many laboratories using this potential biomarker in serum also report the structure incorrectly.

Another problem in the survey arose with *N*-glycoylneuraminic acid (**5/38**), present in the bovine version of α1-glycoprotein. This carbohydrate is antigenic and is of concern to pharmaceutical companies producing pharmaceuticals in organisms that utilize this sialic acid. In the survey, eight of the laboratories, including seven of the eight participating industrial laboratories failed to detect its presence. All of the four laboratories that used a fluorescence tag, failed to detect this sialic acid. Slightly better results were obtained by laboratories using MALDI; of ten labs that used this technique, only two failed to detect this sialic acid. Most laboratories that successfully detected this carbohydrate, permethylated their samples, which, of course, would stabilize it to MALDI conditions. With mixtures containing different quantities of glycans, no lab correctly detected either three or four of the changes, one lab identified two of the four changes, seven labs identified one change but the 11 other labs failed to identify any changes correctly. Clearly, current analytical methods leave much to be desired.

i. Applications of MALDI to the detailed structural determination of N-linked glycans

A large number of reports have appeared on the applications of the above techniques to analysis of *N*-glycans from specific glycoproteins. These are summarized in Tables 10 and 11. Other examples can be found in the tables on medical applications of MALDI MS (Table 23) and biopharmaceuticals (Table 24). Some of the more unusual structures to be discovered are tetra-antennary glycans with poly-*N*-lactosamine extensions with up to nine fucose residues in human seminal plasma (Pang et al., 2009), a $Man_5GlcNAc_2$ glycan with a bisecting GlcNAc residue (**64**) (Buser et al., 2010); a $Man_8GlcNAc_2$-type glycan with two bisecting GlcNAcs (**65**) proposed from *Dictyostelium discoideum* (Schiller et al., 2009; Feasley et al., 2010) and an unusual glycan with internal fucose and glucuronic acid (GlcA) from *Rapana venosa* hemocyanin (Velkova et al., 2009). However, in the latter case, the structure was based on evidence from only one positive ion MS/MS spectrum and is open to alternative interpretations.



64 **65**

Symbols as defined for structures 17 and 18 plus

○ = mannose

j. Miscellaneous studies

Among other studies, MALDI-TOF MS has been used to confirm the glycan compositions of several well-known glycoproteins in a study showing that glycosylation protects proteins against free radicals generated from toxic xenobiotics (Martínek et al., 2010) The rice-derived recombinant human transferrin (rhTF) has been shown to be non-*N*-glycosylated by MALDI and PNGase F enzyme digestion (Zhang et al., 2010a).

3. *O-linked Glycans*

Compared with *N*-glycans, comparatively little has been published on the analysis of *O*-glycans. Two reviews include one on analytical methods for the analysis of MUC-type *O*-linked glycans (Jensen et al., 2010) (137 references) and a second on more general MS-based methods for *O*-glycan analysis (Sheng, Xia, & Yan, 2010).

a. Release of O-Linked glycans

i. β-Elimination. Because there is no general endoglycosidase for release of *O*-glycans, these compounds are usually released chemically. β-Elimination using a strong base such as

TABLE 10. Use of MALDI MS for Examination of *N*-Glycans From Specific Glycoproteins

Glycoprotein	Methods[1]	Notes	Reference
β1,3-*N*-acetyl-glucosaminyl-transferase (human in insect cells and silkworm larvae)	PNGase A, TOF, high-mannose, hybrid glycans (2-AP)	Only 1,6-Fuc in silkworm. Therefore, suitable for producing human glycoproteins	(Dojima et al., 2009)
Alpha-fetoprotein from HepG2 and HuH-7 cells	PNGase F, TOF, QIT-TOF (DHB), (per-Me)	Structural determination and use of lectin array and gene expression (complex glycans)	(Ito et al., 2009a)
Angiotensin-I-converting enzyme, *N* domain; recombinant in CHO cells	Trypsin, PNGase F, TOF/TOF (CHCA), glycopeptide	To study role of glycosylation and crystal structure in complexes with an *N* domain-selective phosphinic inhibitor	(Anthony et al., 2010)
Arylphorin from *Antheraea pernyi* (Chinese oak silkworm)	PNGase F, TOF, glycans (2-AB, per-Me)	Presence of $Glc_1Man_9GlcNAc_2$ at Asn-196-glycan shown to be important for structural stability	(Ryu et al., 2009)
Asialofetuin	TOF (DHB, CHCA) glycans (TMPP derivs)	As standard for development of derivatization method (bi-tri-antennary complex)	(Liu, et al., 2010h)
Attachment glycoprotein from *Hendra* virus	PNGase F, TOF (DHB), glycans, -ve ESI-MS/MS	Structural determination (biantennary complex, bisect)	(Bowden et al., 2010)
Beta2-Glycoprotein 1 (human)	Q-TOF	23 Bi- and tri-antennary complex glycans at Asn-143, 174 and 234	(Kondo et al., 2009)
Beta2-Glycoprotein I (human)	Q-TOF	Use of HILIC LC for glycopeptide fractionation. Results as in row above	(Kondo et al., 2010)
CD24 from mouse brain	PNGase F, TOF/TOF (ATT), glycans (2-AP, per-Me)	Structural determination (high-mannose, hybrid, complex (bi-, tri-, tetra-antennary))	(Bleckmann et al., 2009a)
CD24IgG1 (human in CHO cells)	PNGase F, TOF (DHB), glycans (per-Me)	Structural determination (bi-triantennary)	(Motari et al., 2009)
CD34 from human endothelium	PNGase F, TOF, glycans	Structural identification (biantennary complex)	(Mir et al., 2009)
CEACAM1 (recombinant HEK293 cells)	PNGase F, R-TOF (DHB), ESI (-ve), glycans (free and Me-ester)	Structural determination. High-mannose, complex (bi-, tri-, tetra-antennary) glycans, use of -ve ion ESI-MS/MS	(Harvey, et al., 2009a)
Cell adhesion molecule L1 (recombinant in Sf9 and Tn insect cells)	PNGase A, PNGase F, L-TOF/TOF (DHB)	Optimization of expression system. DMSO shown to increase expression without affecting glycosylation	(Gouveia et al., 2010)
Cellobiohydrolase Cel7A from *Talaromyces emersonii* expressed in *Saccharomyces cerevisiae*	L-TOF (sinapinic), Protein after deglycosylation with Endo F1	Expression of the protein in *Saccharomyces cerevisiae*	(Voutilainen, et al., 2010)
Chaoptin from *Drosophila melanogaster*	Trypsin, PNGase F, L-TOF, TOF/TOF (DHB, CHCA), glycopeptides, glycans (2-AP)	Glycan processing shown to depend on backbone structure of parent peptide. (high mannose)	(Kanie et al., 2009)
C-reactive protein (human)	PNGase F, propionic acid, TOF (DHB), sialic acid	Glycosylated molecular variants shown to activate complement-mediated hemolysis of erythrocytes in TB and Indian leishmaniasis	(Ansar et al., 2009)

(*Continued*)

TABLE 10. (*Continued*)

Cu/Zn-Superoxide dismutase from *Kluyveromyces marxianus* NBIMCC 1984	PNGase F, TOF (DHB), glycans	Structural identification. Man_3-$MeMan_1$-Fuc_1-$GlcNAc_2$	(Moshtanska et al., 2009)
Cu/Zn-Superoxide dismutase from *Kluyveromyces* yeast NBIMCC 1984	PNGase F, trypsin, MALDI (DHB), glycans, glycopeptides	Structural determination ($Man_5GlcNAc_2$ but structure deduced from MS/MS unusual)	(Dolashka-Angelova et al., 2010)
Defibrase from *Agikistrodon acutis* (snake venom)	PNGase F, R-TOF (DHB), HPLC, Glycans (2-AB), exoglycosidases	Structural determination. High-mannose, hybrid, complex (bi-, tri-antennary) glycans	(Luo et al., 2010)
Dopachrome tautomerase (human in Sf9 insect cells)	TOF/TOF (CHCA), glycopeptides	Structural determination (paucimannosidic)	(Vavricka et al., 2010)
E2 glycoprotein (Swine fever in epithelial pig kidney cells)	PNGase F, R-TOF (DHB), ESI-MS/MS (-ve ion), glycans (free and 2-AB)	Structural determination (high-mannose, hybrid, complex (bi-, tri-, tetra-antennary) glycans). Significant amounts of α-Gal	(Montesino et al., 2009)
EmA9 antigen from *Echinococcus multilocularis* (adult worms)	Hydrazine, TOF/TOF (DHB), glycans (2-AB)	Structural determination. High-mannose, complex (bi-, tri-, tetra-antennary)	(Hülsmeier et al., 2010)
Endo-polygalacturonase I from *Stereum purpureum* (recombinant in *Pichia pastoris*)	Endo H, TOF (sinapinic), glycoprotein and Endo H product	Expression, purification, and analyses of glycosylation and disulfide bonds. $Man_{8\text{-}10}GlcNAc_2$	(Ogawa, et al., 2009)
Factor VIII (from CHO cells)	PNGase F, TOF (DHB), glycans (2-AB)	Structural determination (high-mannose, bi-, tri-, tetra-antennary complex)	(Thim et al., 2010)
Factor IX (human from transgenic pig)	PNGase F, R-TOF (DHB) glycans, (acetohydrazide, 2-AA)	Development of amidation technique (see text) and structure determination (bi-, tri-antennary complex)	(Gil, et al., 2010)
$GABA_A$ receptor β2 subunit (from HEK293T cells)	PNGase F, Endo H, TOF	Structural determination (high-mannose, biantennary complex)	(Lo et al., 2010)
γ-Glutamyl transpeptidase (human (renal and hepatic))	PNGase F, TOF/TOF (DHB), glycans (per-Me), LC-MS/MS	Structural determination (68 high-mannose, bi-, tri-, tetra-antennary complex)	(West et al., 2010)
Glycodelin glycomers (human)	PNGase F, TOF/TOF (DHB), glycans (per-Me), GC/MS	Different glycosylation in four glycomers. Two inhibited cell proliferation others did not	(Lee et al., 2009b)
Gp1, sGP from Ebola virus (recombinant in HEK cells)	PNGase F, TOF (DHB), ESI-MS/MS (-ve ion), glycans, exoglycosidase	Structural determination. High-mannose, hybrid, complex (bi-, tri-, tetra-antennary) glycans	(Ritchie et al., 2010b)
Gp64 and gp116 from yellow head virus of *Penaeus monodon* shrimp	PNGase F, R-TOF (DHB), glycopeptides	Site analysis, glycan composition by mass difference	(Soowannayan, et al., 2010)
Gp120 (HIV, expressed in 293T, jurkat, RD, HepG2, CHO cell types)	PNGase F, FT-ICR (DHB), glycans	Comparative structural determination (high-mannose, hybrid, bi-, tri-antennary complex)	(Raska et al., 2010)
Gp120 from HIV	PNGase F, TOF/TOF (DHB), glycans	Structural determination (high-mannose)	(Doores et al., 2010)
Gp120 from HIV	PNGase F, TOF/TOF (DHB), glycans	Structural determination (high-mannose)	(Dunlop et al., 2010)

TABLE 10. (*Continued*)

Gp130 (cell surface glycoprotein from *Dictyostelium*)	PNGase F, PNGase A, Endo H, TOF/TOF (DHB, CHCA, THAP), glycans (2-AB, per-Me), glycopeptides	Structural determination (high-mannose, with bisect on branching mannose and 6-antenna)	(Feasley, et al., 2010)
Gp140 from *Larus crassirostirs* (gull) egg yolk	PNGase F, TOF/TOF (DHB), high-mannose glycans	GnT1-defficient cells gave only high-mannose glycans	(Eggink et al., 2010)
Grass pollen group 1 allergens	PNGase A, TOF (CHCA, DHB), ESI, glycopeptides	Structural determination, paucimannosidic glycans	(Fenaille et al., 2009)
Haptoglobin from *Phoca vitulina* (Harbor seals) Plasma	PNGase F, TOF (DHB), glycans (Per-Me)	Structural determination - mainly biantennary glycans	(Rosenfeld et al., 2009)
Hemagglutinin from Influenza virus grown in HEK293 cells	Endo H, MALDI, glycans	Glycans shown to affect receptor binding and immune response	(Wang et al., 2009a)
Hemocyanin from *Rapana venosa*	PNGase F TOF/TOF, glycans (per-Me, amide), ESI	Structural determination (mainly composition) Contain Me-Man	(Dolashka, et al., 2010)
Hemocyanin from *Rapana venosa*	PNGase F, TOF, ESI, glycans	Structural determination. Ident. of novel glycan with internal fucose and glucuronic acid	(Velkova, et al., 2009)
HIV-1 (Clade C) Envelope proteins (recombinant in 293T cells)	PNGase F, TOF/TOF (DHB/CHCA), LC-ESI-MS/MS, glycans	Structural determination. High-mannose, hybrid, complex (bi-, tri-, tetra-antennary glycans). Clade-specific glycosylation	(Go et al., 2009)
HIV-1 V3 Glycopeptide domain fused with human IgG1-Fc (recombinant in HEK293T cells)	PNGase F, TOF (DHB)	Structural determination (complex, bi-, tri-, tetra-antennary). Use of glycosidase inhibitors to change profile.	(Yang et al., 2010f)
Honey bee venom	L-, R-TOF/TOF, glycoprotein	Structural determination, (paucimannosidic glycans). Detection in envenomed tissue	(Francese et al., 2009b)
Horseradish peroxidase (HRP)	MALDI-MS/MS, ESI-MS/MS, glycopeptides	Structural determination of HRP as model (in Chinese)	(Chen et al., 2010d)
Horseradish peroxidase (HRP)	Trypsin, QIT-TOF (DHB), glycopeptides	As model for testing nanodevice for enzyme immobilization	(Qian, et al., 2010)
Human leukocyte receptor IIIa (FcγRIIIa) in CHO/DG44 cells	PNGase F, TOF/TOF (s-DHB, THAP), glycans	Effect of *N*-glycosylation on binding to IgG antibodies	(Shibata-Koyama et al., 2009)
Hyaluronidase (Ves v 2) from *Vespula vulgaris* (Yellowjacket)	PNGase F, TOF, LC/MS, glycans	Structure. *N*-glycans needed for human antibody recognition	(Seppälä et al., 2009)
IgG from *Larus crassirostirs* (gull) egg yolk	PNGase F, TOF, TOF/TOF, Q-TOF, ESI, glycans -2-AP, per-Me)	Structural determination. Complex (bi-, tri-antennary) glycans	(Suzuki et al., 2009b)
IgG (human)	TOF/TOF (CHCA)	Decreased levels of bisecting GlcNAc glycoforms shown to be associated with human longevity	(Ruhaak et al., 2010d)
IgG (human)	PNGase F, TOF (DHB), Glycans, -ve ESI-MS/MS	Glycan release in the presence of DTT produces reducing-terminal -SH artefacts	(Harvey & Rudd, 2010)
IgG (mouse)	Trypsin, PNGase F, TOF (DHB), glycans (per-Me)	Mannose receptor shown to interact with Fc receptors. Critical for the development of crescentic glomerulonephritis	(Chavele et al., 2010)
IgG2b (mouse)	Trypsin, TOF (CHCA), FAB, ESI, glycopeptides	Mutational deglycosylation of the Fc portion shown to cause *O*-sulfation of Tyr adjacent to the originally glycosylated site	(Masuda et al., 2010)

(*Continued*)

TABLE 10. (*Continued*)

IgM (heavy chain) from Nurse shark	PNGase F, R-TOF (DHB), ESI (-ve), glycans	Structural determination, bisected complex glycans α-Gal	(Harvey et al., 2009d)
Inducible co-stimulator (recombinant, CHO-K1 and Jurkat cells)	PNGase F, TOF (DHB), glycans (2-AA)	Of three glycosylation sites, N23, N89, N110, only glycans at N89 required for proper folding	(Kamei et al., 2010)
Intercellular adhesion molecule-5 (ICAM-5) from adult rat brain	PNGase F, QIT-TOF, High-mannose, hybrid, complex glycans (ABOE)	Structural determination and comparison with other ICAMs. Less branching. More high-Man	(Ohgomori et al., 2009)
Interferon-γ (CHO cells)	MALDI (no details)	Investigation of glycosylation genetics. (high-mannose, hybrid, complex glycans, no bisects)	(Wong et al., 2010a)
JlpA (surface-associated lipoprotein) from *Campylobacter jejuni*	Trypsin, TOF, glycopeptides	Asn-107, 146. Glycan ident. earlier, detected by mass difference. $HexNAc_5Bac_1Hex_1$	(Scott et al., 2009)
Keyhole limpet hemocyanin	PNGase F, R-TOF/TOF (ATT), glycans	For development of protein binding assay.	(Wuhrer et al., 2010)
Lactoferrin from human milk	PNGase F, FT-ICR, glycans, peptides	Lactoferrins shown to be glycosylated during first 10 days of lactation (fucosylated $Hex_5HexNAc_4$)	(Froehlich et al., 2010)
Lactophorin (GlyCAM-1) from bovine milk	PNGase F, QIT-TOF (DHB), glycans (2-AP)	Structural determination. (complex bi-, tri-antennary)	(Inagaki et al., 2010)
Lipocalin 2 Lactoferrin from mouse uterine luminal fluid	Trypsin, PNGase F, TOF/TOF (DHB), glycans (per-Me)	Highly fucosylated with Lewis X and Y epitopes. High-mannose, complex	(Kuo et al., 2009)
L-Selectin (human in HEK293F cells)	PNGase F, TOF (D-arabinosazone, ATT), glycans (per-Me), Exoglycosidase	Structural determination (68 complex, sulfated GalNAc-GlcNAc)	(Wedepohl et al., 2010)
Machupo virus attachment glycoprotein (recombinant in HEK 293T cells)	PNGase F, R-TOF (DHB), glycans, ESI (-ve)	Structural determination, (high-mannose, hybrid, complex glycans). Crystal structure	(Bowden et al., 2009)
Mannose receptor from mouse spleen	PNGase F, TOF (DHB), LC-ESI-MS	Structural determination. (complex, bi-, tri-antennary). Tissue-specific sialic acid linkage	(Su et al., 2009)
Myeloperoxidase (human recombinant in CHO cells)	PNGase F (in gel), R-TOF, LC-ESI-MS, glycans (per-Me)	Structural determination (complex, high-mannose). Glycosylation required for optimal enzymatic activity	(Van Antwerpen et al., 2010)
Myeloperoxidase (human cancer patients)	Q-TOF (DHB), Glycopeptides. Glycans by Orbitrap MS/MS	Structural determination	(Ravnsborg et al., 2010a)
Nipah virus fusion protein recombinant in 293T cells	Trypsin PNGase F, TOF/TOF (DHB), glycans (per-Me)	High-mannose, hybrid, bi-, tri-antennary complex. Binding to endothelial galectin 1	(Garner et al., 2010)
Omega-1 from *Schistosoma mansoni*	Trypsin, R-TOF/TOF (DHB), glycopeptides, ESI, Exoglycosidase	Structural determination (biantennary complex with Lewis X motif)	(Meevissen et al., 2010)
Orosomucoid (α1-acid glycoprotein, human)	PNGase F, TOF/TOF (DHB), glycans (per-Me)	Study of high-affinity glycoprotein-receptor interactions using engineered ligands. (complex, bi-, tri-, tetra-antennary) glycans	(Coombs et al., 2010)

TABLE 10. (*Continued*)

Ovalbumin from chicken	TOF (DHB, CHCA) glycans (TMPP derivs.)	As standard for development of derivatization method (high-mannose, hybrid, complex)	(Liu, et al., 2010h)
Ovalbumin from chicken	Hydrazine, TOF	To study carbohydrate to carbohydrate interactions	(Utkina et al., 2010)
Ovomucoid Ovotransferrin from *Larus crassirostirs* (gull) egg yolk	PNGase F, TOF, TOF/TOF, Q-TOF, ESI (Orbitrap), glycans -2-AP, per-Me)	Structural determination. (Complex, bi-, tri-, tetra-antennary). Glycans with Gal-α-(1→4)-Gal	(Suzuki, et al., 2009b)
Pectin methylesterase from *Ficus awkeotsang* (Jelly fig) achenes	Trypsin PNGase F, TOF/TOF (DHB), glycans (per-Me)	Structural determination (paucimannosidic, truncated complex glycans). Site analysis (Asn-153)	(Hsiao et al., 2009)
Peroxidase from *Arabidopsis thaliana*	HF, L-, R-TOF, TOF/TOF, Glycopeptides	Paper mainly on proteins. Paucimannosidic glycan structures assumed by mass difference following HF.	(Albenne et al., 2009)
Phaseolin from French bean	PNGase A, Endo H, TOF/TOF (DHB), glycans, LC-MS, glycopeptides	Structural determination. Glycans contribute significantly to physico-chemical properties	(Kimura et al., 2010)
Phospholipase A2 from *Agkistrodon blomhoffii Ussurensis* (Chinese snake) venom	PNGase F, TOF (sinapinic), glycopeptide	Mainly ESI. MALDI-TOF to determine mass of glycan (581 Da) after removal by PNGase F. No structural details other than it contained GlcNAc.	(Liu et al., 2009g)
Phytohemagglutin from *Phaseolus vulgaris* (common bean)	PNGase F, TOF, ESI, glycans (per-Me)	Glycans: High-Man, paucimannosidic. As model for study of proteomic approaches to lectin structure and function	(Nasi et al., 2009)
Procyclins from *Trypanosoma brucei*	TOF, glycoprotein, glycopeptides	Structure confirmation (high-mannose)	(Clemmens et al., 2009)
Progranulin recombinant in COS7 cells	PNGase F, TOF/TOF (DHB), glycans (per-Me), ESI MS/MS	Structural determination (biantennary complex)	(Songsrirote et al., 2010)
Proline-rich proteins from human saliva	TOF/TOF, glycoproteins	Identification of new post-translational modifications	(Vitorino et al., 2010)
Prolyl endoprotease from *Aspergillus niger*	PNGase F, R-TOF, TOF/TOF (CHCA, DHB, ATT di-NH_4 hydrogen citrate), PSD	Structural determination (high-mannose) and evaluation of the enzyme for its possible application in proteomics	(Šebela et al., 2009)
Pst1 from *Saccharomyces cerevisiae*	Endo H, TOF, glycans	Shown to bind to HIV antibody 2G12 and to inhibit gp120 interactions (glycans -high-Man)	(Luallen et al., 2009)
Ribonuclease B	TOF (DHB, CHCA) glycans (TMPP)	As standard for development of deriv. method (high-Man)	(Liu, et al., 2010h)
SARS-CoV spike glycoprotein from African green monkey	PNGase F, TOF (DHB), ESI-MS/MS (-ve ion), glycans, exoglycosidase	Structural determination. (high-mannose, hybrid, complex, bi-, tri-, tetra-antennary)	(Ritchie et al., 2010a)
S-layer glycoprotein from *Haloferax volcanii* (archaeon)	Trypsin, R-TOF/TOF (CHCA), glycopeptide	Involvement of AglF and AglM proteins in glycan synthesis. Pentasaccharide	(Yurist-Doutsch et al., 2010)

(*Continued*)

TABLE 10. (*Continued*)

S-layer glycoprotein from *Haloferax volcanii*	Proteinase K, TOF, LC/MS	AglJ shown to add the first sugar of the *N*-linked pentasaccharide Structural determination.	(Kaminski et al., 2010)
Stabilin-2 (HARE) from human 190-HARE ecto-domain	PNGase F, R-TOF, TOF/TOF (DHB), glycans (per-Me)	Glycans needed for hyaluronan binding to ecto-domain, but not for cellular endocytosis of hyaluronan	(Harris et al., 2010a)
Stem cell marker 19A from mutant HEK 293T cell line	PNGase F, R-TOF (DHB), ESI (-ve), glycans	Production of Lec36 cell line deficient in α-mannosidase II	(Crispin et al., 2009b)
Subtilase SlSBT3 from tomato	Trypsin, TOF/TOF, glycopeptides	Structure:function determination. Glycans: complex, paucimannosidic	(Cedzich et al., 2009)
Swine fever E2 glycoprotein recombinant from goat milk	PNGase F, TOF (DHB), -ve, ESI-MS/MS	Structural determination (bi-, tri-antennary complex, hybrid, high-mannose)	(Montesino et al., 2010)
Synaptic cell adhesion molecule SynCAM 1 from mouse brain	Trypsin, PNGase F, TOF, glycopeptides	SynCAM1 shown to be a target for polysialylation	(Galuska et al., 2010c)
Thrombin-activatable fibrinolysis inhibitor from bovine plasma	Trypsin, TOF/TOF, Q-TOF (DHB), glycopeptides	Structure determination (biantennary complex). Similar to human enzyme	(Valnickova et al., 2009)
Tissue factor pathway inhibitor from human plasma	V8 protease, cyanogen Br, L-TOF (DHB), glycopeptides	Biochemical characterization. Proposed bi- and tri-antennary glycan structures	(Mori et al., 2009b)
Tissue plasminogen activator (recombinant)	PNGase F, TOF (DHB), glycans (ANSA derivs)	Development of ANSA derivatization (complex glycans)	(Briggs, et al., 2009)
Variant surface glycoprotein MITat1.8 from *Trypanosoma brucei* (Lister strain 427)	Pronase, TOF, glycopeptides (per-Me)	Structural determination (biantennary complex)	(Mehlert et al., 2010)
Vascular endothelial growth factor 165 (VEGF165), (human in Sf 21 insect cells)	PNGase F, TOF (DHB), glycans	Development of CE-MS method for analysis of the glycoprotein. (high-mannose glycans)	(Puerta & Bergquist, 2009)
Vitellogenin from *Macrobrachium rosenbergii* (prawn)	PNGase F (in gel), TOF (DHB), ESI-MS/MS	Structural determination. (high-mannose). Site analysis (N-151, 159, 168, 614, 660, 2300)	(Roth et al., 2010)

[1]Format (not all items present): Glycan release method and/or protease, MALDI method (matrix), compounds run (derivative), other methods.

sodium hydroxide followed by reduction to prevent a peeling reaction is the most common method but has the disadvantage of eliminating the reducing terminus, thus preventing tagging with fluorescent or other tags. Some investigators have, thus, investigated the use of milder bases with the aim of avoiding the reductive stage and retaining the reducing terminus. Zheng, Guo, and Cai (2009) have compared ammonia, methylamine and dimethylamine at 55°C for 6 hr for release of *N*-acetylgalactosamine (GalNAc) from a small glycopeptide. β-Elimination with dimethylamine and methylamine resulted in the conversion of the glycopeptide to 69.2% of the dimethylamine derivative at *m/z* 550.32 and 61.5% of the methylamine derivative at *m/z* 543.33, respectively. However, the incubation of the glycopeptide with ammonia only resulted in 8% production of the product. The authors concluded that elimination with dimethylamine was the most efficient for release the *O*-linked glycans. Release with methylamine was used by Sun et al. (2010b) to determine the glycosylation sites in human protein C inhibitor by the 13.03 mass increment introduced by the reaction.

Release with ammonia has been investigated in detail by Yu et al. (2010a) for *O*-glycan chains with β1,3-linked cores. In contrast to β1,4-linkages of the *N*-glycan-type, which were shown to be stable under the ammonium-based alkaline conditions, the β1,3-linkage was found to be labile and to give considerable peeling (Yu et al., 2010a). The results indicated that complete prevention of peeling under nonreducing alkali-catalyzed hydrolysis conditions remains difficult. The yields of *O*- and *N*-glycans from bovine fetuin released by conventional means (PNGase F and reductive β-elimination with NaOH) were found to be greater. It was concluded that great care should be taken when employing such non-reducing alkaline conditions in glycomic analysis and in obtaining some *O*-glycans for functional studies.

Because the hydroxide ion appears to cause the unfavorable peeling reactions, Miura et al. (2010b) have investigated the use of the ammonium salt, ammonium carbamate for glycan release. The efficiency of release with ammonium carbamate was compared with a common conventional procedure, namely saturated ammonium carbonate/aqueous ammonia with bovine submaxillary mucin (BSM) as the test compound. Release with ammonium carbamate did not exhibit significant loss of GlcNAc-β1,3 (Neu5Acα2,6)GalNAc or GlcNAcβ1,3(Neu5Gcα2,6)GalNAc

TABLE 11. Use of MALDI MS for Examination of *N*-Glycans From Intact Organisms, Tissues or Glycoprotein Mixtures

Source	Methods[1]	Notes	Reference
Arabidopsis thaliana (Seedlings)	Endo H, TOF (DHB), high-mannose glycans	*N*-glycan trimming by glucosidase II shown to be essential for *Arabidopsis* development	(Soussilane et al., 2009)
Arabidopsis thaliana (Leaves, wild type and mutants)	TOF (DHB), glycans (2-AP)	Genetics of mannosidases. Golgi α-mannosidase I responsible for plant *N*-glycan maturation	(Kajiura et al., 2010b)
Arabidopsis thaliana	Hydrazine, TOF (DHB), glycans (2-AP)	ALG3 mutant shown to synthesize immature glycans in the ER and to accumulate unique *N*-glycans (high-mannose, paucimannosidic)	(Kajiura et al., 2010a)
Arabidopsis thaliana (Leaves)	PNGase A, R-TOF/TOF (DHB), glycans	Determination of the role of *LEW3* encoding a putative α-1,2-Man-transferase	(Zhang et al., 2009e)
Biomphalaria glabrata (Snail), (Hemolymph glycoproteins)	Hydrazine, R-TOF/TOF (ATT), glycans (2-AP)	Structural determination in strains with different susceptibility to *Schistosoma mansoni* infection (Paucimannosidic)	(Lehr et al., 2010)
Caenorhabditis elegans	PNGase A and F, TOF/TOF (DHB), glycans (2-AP)	Paucimannosidic with Gal-Fuc on core which confers sensitivity towards nematotoxic fungal galectin CGL2	(Butschi et al., 2010)
Chardonnay white wine (Glycoproteins)	L-TOF/TOF (DHB), glycopeptides	To determine glycoproteomic profile	(Palmisano et al., 2010)
Dogs and cats (Lungs)	PNGase A, TOF, glycans (2-AP)	Structural determination in animals susceptible to H5N1 influenza (high-mannose, bi-, tri-antennary complex).	(Thongratsakul et al., 2009)
Chelonia mydas (Sea turtle), (eggs)	PNGase A, TOF (DHB), glycans (2-AP)	38% of *N*-linked glycans carry Gal-α-(1→4)-Gal epitopes, similar to birds	(Yagi et al., 2010)
Chicken (Eggs, yolk and white)	Hydrazine, TOF (DHB), glycans (2-AP), HPLC	To produce large amounts of *N*-glycans (high-Man, truncated complex in white, bi-, tri-antennary in yolk)	(Sumiyoshi et al., 2009)
Chinese hamster (Glycoproteins from Lec15.Lec1 mutants)	PNGase F, R-TOF, TOF/TOF (DHB, arabinosazone), glycans (per-Me)	To investigate action of the glycoprotein, Large	(Aguilan et al., 2009)
Chinese hamster (K1 cells)	PNGase F, TOF	Deletion of FUT8 gene yields cells that produce completely non-fucosylated antibodies	(Malphettes et al., 2010)
Chinese hamster mutants (Cellular glycoproteins)	PNGase F, TOF, TOF/TOF (DHB), glycans (per-Me), GC/MS	Structural determination of glycans from Lec mutants. High-mannose, complex (bi-, tri-antennary, *N*-Ac-Lac extensions)	(North et al., 2010a)
Coprinopsis cinerea (Basidiomycete), (Fruiting body)	PNGase F, TOF/TOF (DHB), glycans (2-AB)	Identification of high-mannose glycans and $Man_5GlcNAc_2$ with additional bisecting GlcNAc.	(Buser, et al., 2010)
Danio rerio (Zebrafish), (Embryos)	PNGase F, R-TOF/TOF (DHB), glycans (per-Me)	Developmental regulation of oligo-sialylation	(Chang et al., 2009)
Dictyostelium discoideum (Slime mould), (Cultures or secreted proteins)	PNGase A and F, Endo H, TOF/TOF (DHB), LC-MS, GC/MS, glycans (2-AP)	Structural determination (high-mannose, bisected high-mannose glycans). Development associated with alteration of fucosylated glycans	(Schiller, et al., 2009)
Gallus gallus domesticus (Chicken), (Embryonated eggs (10-days))	PNGase A, TOF, glycans (2-AP), exoglycosidase digestions	Analysis of sialic acid linkage in relation to binding of human and avian influenza viruses. High-mannose, hybrid, complex	(Sriwilaijaroen et al., 2009)

(*Continued*)

TABLE 11. (*Continued*)

Helicobacter pullorum (Membranes)	TOF/TOF, glycopeptides	Structural determination, linear pentasaccharide	(Jervis et al., 2010)
Human, bovine (HL60s and MDBK cells)	PNGase F, Free oligo-saccharides, TOF (DHB), glycans (2-AA)	Novel mannosidase inhibitors used to probe glycoprotein degradation pathways in cells	(Butters et al., 2009)
Human (Embryonic stem cells)	PNGase F, TOF/TOF, glycans (free and per-Me)	Glycan profile changes with cell differentiation. High-mannose, complex, glycans	(Satomaa et al., 2009b)
Human (Neutrophils)	PNGase F, TOF, TOF/TOF (DHB glycans (per-Me)	Structural determination of samples from geographically remote labs. Similar high-Man, hybrid, complex	(Babu et al., 2009)
Human (Myocytes from adult atria and ventricles)	PNGase F, TOF, TOF/TOF, glycans (Per-Me)	Aberrant glycosylation modulates cardiac electrical signalling in e.g. Chagas disease, Complex glycans.	(Montpetit et al., 2009)
Human (Brush boader, enterocyte-like HT-29 cells (clone 5M12))	Trypsin PNGase F, TOF, glycans (per-Me), ESI, GC/MS	Structural determination and involvement of complex-type *N*-glycans in apical trafficking	(Morelle et al., 2009b)
Human (Mesenchymal stem cells from bone marrow)	PNGase F, R-TOF/TOF, FT-ICR (DHB), glycans (per-Me)	Structural determination. (High-mannose, hybrid, complex glycans). Can be used to evaluate cellular differentiation stage	(Heiskanen et al., 2009)
Human (Lung)	PNGase F, R-TOF, TOF/TOF, glycans (per-Me)	DAS181 (potential therapeutic) inhibits H5N1 flu infection by desialylation of complex glycans	(Chan et al., 2009b)
Human (Seminal plasma)	PNGase F, TOF/TOF (DHB), glycans (per-Me)	Structural determination (high-mannose, hybrid, complex glycans). Poly-fucosylation	(Pang, et al., 2009)
Human (HT-29 5M12 colon cancer cells)	PNGase F, TOF, glycans (per-Me)	Pattern of *N*-glycosylation serves as a recognition signal for galectin-4. High-Man, hybrid, bi-, tri- tetra-antennary.	(Stechly et al., 2009)
Human (Cytolytic T lymphocytes)	PNGase F, TOF/TOF (DHB), glycans (per-Me)	Loss of effector function shown to be accompanied by major changes in *N*- and *O*-glycosylation	(Antonopoulos et al., 2012)
Marmota monax (woodchuck with liver cancer), (Serum)	PNGase F, Q-TOF (DHB, ATT), glycans (per-Me or phenylhydrazone)	Structural determination. Glycosylation differed from that in cancerous mice	(Lattová et al., 2009)
Mouse (Pluripotent embryonic stem cells)	PNGase F, TOF/TOF (DHB), Glycans (per-^{13}C-Me)	Structural determination of Con A-extracted glycoproteins (high-Man, hybrid, bi-, tri-antennary)	(Alvarez-Manilla, et al., 2010b)
Mouse (WT and ES cells)	PNGase F, TOF/TOF (DHB), glycans (per-Me)	Molecular chaperone Cosmc essential for correct protein *O*-glycosylation. Does not affect *N*-glycans	(Wang et al., 2010c)
Mouse (GlcNAc-T IVa and IVb deficient), (Various tissues)	PNGase F, TOF/TOF (DHB), glycans (per-Me), GC/MS	Elimination of 4-branch of 3-antenna. Preservation of terminal moieties. Compensation mechanism	(Takamatsu et al., 2010)
Mouse and human (Dermis and epidermis)	PNGase F, R-TOF/TOF (DHB), glycans (Me esters)	Gal-α-(1→3)-Gal in mouse epidermis but GalNAc-β-(1→4)-GlcNAc in human. High-mannose, hybrid complex	(Uematsu et al., 2009)
Nicotiana tabacum	PNGase A PNGase F, TOF/TOF (DHB/3% *N,N*-di-methylaniline), ESI-MS/MS	Plants engineered to produce Lewis X epitopes. (Paucimannosidic glycans)	(Rouwendal et al., 2009)

TABLE 11. (*Continued*)

Nicotiana tabacum (Glycoproteins)	PNGase A, R-TOF, glycans	Incorporation of GlcNAc-transferase III, to form bisects, inhibits paucimannosidic glycans	(Frey et al., 2009)
Phasianus versicolor, (Japanese pheasant), (Eggs)	Hydrazine, TOF (DHB), glycans (2-AP)	Structural determination. High-Man, hybrid, bi-, tri-, tetra-antennary complex	(Sumiyoshi et al., 2010)
Rabbit and chicken (Erythrocytes)	TOF, glycans (2-AP)	To study alterations in receptor-binding properties of H1-type swine influenza viruses in embryonated chicken eggs. High-Man, hybrid, bi-, tri-antennary	(Takemae et al., 2010)
Rat (Serum and bile)	Hydrazine, R-TOF/TOF, QIT (DHB), glycans (2-AP)	Study of changes in fucosylation in hepatocarcinogenis	(Nakagawa et al., 2010)
Rat (Hepatocytes, liver epithelial cells)	PNGase F, TOF, glycans (2-AP)	In study of search for biomarkers for hepatic progenitor cells. (High mannose, hybrid glycans)	(Sasaki et al., 2009c)
Rice (Suspension cultures)	Trypsin/PNGase A, TOF (DHB), glycans (2-AP)	Structural determination (paucimannosidic)	(Shin et al., 2010)
Saccharomyces cerevisiae	TOF (DHB), Free high-mannose glycans (2-AP)	To monitor glycoprotein endoplasmic reticulum-associated degradation	(Hirayama et al., 2010)
Schizophyllum commune (Mushroom)	PNGase F, TOF/TOF, glycans	Genomic and biochemical analysis (high-mannose glycans)	(Berends et al., 2009)
Sf 21 cells (Glycoproteins)	Hydrazine, TOF, glycans (2-AP)	Insertion of GlcNAc-II transferase gene produces bisected glycans that retain GlcNAc-T I attached GlcNAc	(Okada et al., 2010b)
Sus domestica (Domestic pig), (Zona pellucida)	PNGase F (on-blot), TOF (DHB, THAP), TOF/TOF (D-arabinosazone)	Structural determination. (Neutral = high-Man, biantennary, acidic = sulfated and sialylated tri-, tetra-antennary glycans). Less sulfation detected than suggested by literature	(von Witzendorff et al., 2009)
Sus domestica (Endothelial and islet cells)	PNGase F, TOF (DHB), glycans (free, 2-AA, per-Me)	Detection of α-Gal and Neu5Gc (human antigens important for tissue transplantation)	(Kim et al., 2009d)
Sus domestica (Corneal endothelial cells and keratocytes)	PNGase F, TOF (DHB), glycans (per-Me, Girard's T)	Structural determination (high-mannose, hybrid, complex glycans) Girard's T for quantitation	(Kim, et al., 2009c)
Sus domestica (Respiratory epithelial cells)	PNGase F, TOF, TOF/TOF (DHB), glycans (per-Me)	Influenza virus shown to utilise α2→6-linked Neu5Ac to infect cells	(Bateman et al., 2010)

[1]Format (not all items present): Glycan release method and/or protease, MALDI method (matrix), compounds run (derivative), other methods.

and the profile of the major *O*-glycans was similar to that obtained following conventional reductive amination with $NaOH/NaBH_4$. On the other hand, glycans obtained by treating BSM with ammonium carbonate/28% aqueous ammonia and analyzed by MALDI-TOF MS showed a significant increase of the disaccharide components, Neu5Acα2,6GalNAc and Neu5Gcα2,6GalNAc, suggesting the presence of a peeling reaction. Use of ammonium carbamate, thus, appears to produce efficient release without concomitant peeling. The release was performed by addition of powdered ammonium carbamate and incubation for 20 hr at 60°C.

Yamada et al. (2009) have used a recently developed automated release apparatus using lithium hydroxide to obtain *O*-glycans from leukemia and epithelial cancer cells. Because these cells usually contain free glycans, the investigators first reduced these with sodium borohydride and then labeled the released glycans with 2-AA in order to avoid interference.

A new release method reported by Goetz, Novotny, and Mechref (2009a) combined enzymatic and chemical techniques and used β-elimination to cleave glycans from serine (Ser) and threonine (Thr) but not Asn. The method involved first a nonspecific proteolysis with pronase, followed by solid-phase

permethylation with sodium hydroxide. The basic sodium hydroxide caused the glycans to be released by β-elimination and these were immediately permethylated. This combination of the enzymatic and chemical procedures was reported to give a substantial improvement in sensitivity and analytical reproducibility over existing methods by minimizing sample losses. Moreover, the approach was reported to extend the cleavage protocols to large glycoproteins where small oligosaccharides were not accessible to conventional chemical treatment. The method was developed with fetuin and used to identify new *O*-glycans from bile salt-stimulated lipase (BSSL).

Maniatis, Zhou, and Reinhold (2010) have released *O*-glycans with aqueous dimethylamine in the presence of sodium borohydride by use of a microwave oven. The release was performed at 70°C and, for a heptapeptide carrying a GlcNAc group attached to Thr, was complete in 70 min. The reaction also labeled the site of detachment with a dimethylamino group. Use of a 1:1 mixture of dimethylamine and $[^2H_3]_2NH$ produced doublets in the peptide mass spectrum separated by six units, allowing the glycosylation sites to be readily identified.

N-Glycans are frequently removed from glycoproteins before *O*-glycan removal by β-elimination. However Stone et al. (2009) have reported improved recovery of *O*-glycans from murine tissues without prior *N*-glycan removal. KBH_4 and KOH were used to remove the *O*-glycans and possible low levels of concomitantly released *N*-glycans were tolerated.

ii. Use of hydrazine. Hydrazine has also been used to release these glycans with a new gas-phase method using anhydrous hydrazine being evaluated by Goso, Tsubokawa, and Ishihara (2009) with MUC-type oligosaccharides from porcine gastric mucin (PGM) and bovine fetuin. Released glycans were examined by HPLC and MALDI-TOF as 2-AA derivatives. Glycans obtained by the treatment with hydrazine at 65°C for 6 hr resembled those obtained by β-elimination, except for the additional disaccharide fractions derived from the core 1 side of the oligosaccharides by further degradation. The other degraded products derived from the core 2 side could not be derivatized by 2-AA, therefore, were not visible by fluorescence detection. Release of the glycans was incomplete after 6 hr but almost complete liberation was achieved by extending the treatment to 18 hr. However, degradation increased. In this case, the addition of barium oxide to the reaction vessel decreased the degree of further degradation. Results similar to PGM were obtained from bovine fetuin, but with less degradation. Application of this method to the analysis of rat gastric mucin (RGM) showed that RGM has a large oligosaccharide portion on the core 1 side.

iii. Other methods. A new method for *O*-glycan removal for study of the residual deglycosylated protein has been reported (Hanisch et al., 2009). Desialylated glycoproteins whose sugar chains consisted of Gal-GalNAc, were immobilized on alkali-stable, reversed-phase Poros 20 beads and treated with periodate to oxidize the *cis*-glycol groups in the Gal residue. The resulting aldehydes were then susceptible to β-elimination under mild (NH_3) basic conditions. The remaining GalNAc residue, which now contained a *cis*-glycol group, was oxidized with further treatment with periodate and removed with base. Although the number of cycles required depended on the number of Gal-GalNAc repeats, large core 2-type glycans that usually only have Gal attached to the 3-position of the core GalNAc, could be deglycosylated in only two steps.

O-Linked glycosylation often occurs in MUC-type domains that are heavily and heterogeneously glycosylated. Several strategies to determine the heterogeneity of these domains have recently been investigated with four glucanases secreted in large quantities from *Trichoderma reesei*, all of which contained heavily *O*-glycosylated MUC-like linker regions, being used as models. The strategies involved monosaccharide compositional analysis and identification of the released glycans by HPAEC-pulsed amperometric detection (PAD) and carbon-LC ESI-MS/MS. Glycosylated peptides were generated by different protease digestions (trypsin, papain, Asp-N, PreTAQ) and enriched by HILIC microcolumns. The complex *O*-glycan heterogeneity was determined by MALDI-MS and ESI-MS, but the dense *O*-glycosylation in the MUC-type domains conferred high resistance to protease cleavage. ETD-MS/MS of the glycopeptide-enriched protease digests was unsuccessful for the assignment of *O*-glycosylation at individual sites within the MUC-type domains but allowed several previously unknown *O*-linked sites outside the defined linker region to be found on two of the four glucanases (Christiansen et al., 2010).

iv. Comparison of methods. Three samples of IgA1 isolated from the serum of patients with multiple myeloma have been distributed on behalf of the Human Proteome Organization Human Disease Glycomics/Proteome Initiative to 15 laboratories for comparative analysis of their *O*-glycans. A range of techniques was used; the two strategies that yielded the best data were direct positive ion MS analysis of permethylated glycans and LC-MS analysis of native reduced glycans in negative ion mode. The studies reinforced the pre-eminent performance of MS techniques for *O*-glycan profiling (Wada et al., 2010b).

b. Applications of MALDI to the structural determination of O-linked glycans

Examples of the application of MALDI MS to the analysis of *O*-glycans are summarized in Tables 12 and 13.

4. Glycosaminoglycans

Several reviews and general analytical methods have been reported; these are listed in Table 14.

Loss of sulfate is a major problem in the MALDI analysis of these compounds but this can be avoided by use of desorption ESI (Przybylski et al., 2010a). Little use appears to have been made of the peptide binding method for stabilization of sulfate groups in these compounds as reported by Juhasz and Biemann (1994). One report concerns the identification of a pentasulfated hexasaccharide responsible for binding to the growth factor pleiotrophin (Li et al., 2010a). The compound was complexed with $(Arg\text{-}Gly)_{15}$ and identified by MALDI-TOF from DHB. In another study (Li et al., 2010a), a pentasulfated hexasaccharide with a novel structure ($\Delta^{4,5}$HexAα1-3GalNAc(4S)β1-4IdoA(2-S)α1-3GalNAc(4S)β1-4IdoA(2S)α1-3GalNAc(4S)) has been isolated from the chondroitinase AC-I digest of shark skin. Again, $(Arg\text{-}Gly)_{15}$ was used as the complexing agent.

Bultel et al. (2010) have developed a method for analysis of heparin oligosaccharides by using controlled nitrous acid degradation followed by high-performance anion exchange chromatography (HPAEC) separation and UV-MALDI-TOF analysis. The use of three different matrices, DHB, CHCA, and *nor*-harmane were investigated but only DHB and *nor*-harmane were needed to assign the position of sulfate groups. DHB

TABLE 12. Use of MALDI MS for Examination of *O*-Glycans From Specific Glycopeptides

Glycoprotein and source	Methods[1]	Notes	Reference
Angiopoietin-like protein 3 (ANGPTL3), (In CHO IdID cells)	Trypsin, TOF (DHB) glycopeptides	*O*-Glycosylation shown to modulate proprotein convertase activation of ANGPTL3	(Schjoldager et al., 2010)
ART v 1 from *Ambrosia artemisiifolia* (ragweed)	$BaOH_2$ release, TOF/TOF (DHB), ESI	Characterization of allergen. Glycans attached to OH-proline. Arabinogalactans	(Léonard et al., 2010)
Bile salt-stimulated lipase from human milk	Combined β-elimination and per-Me, TOF/TOF (DHB), glycans (Per-Me	Development of new combined chemical and enzymatic glycan release method	(Goetz, et al., 2009a)
CD24 from mouse brain	*O*-sialoglycoprotein endopeptidase β-elimination, TOF/TOF (ATT), glycans (per-Me), ESI-MS/MS, GC/MS	Structural determination. (Mucin type and *O*-mannosyl glycans)	(Bleckmann et al., 2009b)
CD24IgG1 (Human in CHO cells)	β-Elimination, TOF (DHB), glycans (per-Me)	Structural determination (Core 1 and 2)	(Motari, et al., 2009)
CD34 from human endothelium	β-Elimination, TOF, glycans	Structural identification (Core 1 and 2)	(Mir, et al., 2009)
α-Crystallin A (reference compound)	TOF (DHB), LC-MS/MS	Development of hydrazide capture method (GlcNAc)	(Klement, et al., 2010)
Ebola virus in HEK cells	Hydrazine, TOF (DHB), ESI-MS/MS (-ve ion), glycans	Structural determination. Core 1, core 2	(Ritchie, et al., 2010b)
EmA9 antigen from *Echinococcus multilocularis* adult worms	Hydrazine, TOF/TOF (DHB), glycans (2-AB)	Structural determination. Unusual *O*-glycan ($Gal_1HexNAc_{1-3}$)	(Hülsmeier, et al., 2010)
Flagellin from *Pseudomonas syringae* pv. *Tabaci* 6605 mutant	Lysyl endopeptidase, TOF/TOF (DHB), glycopeptides	Analysis of genes involved in synthesis of modified 4-amino-4,6-di-deoxyglucose (viosamine)	(Nguyen et al., 2009a)
Flagellin from *Pseudomonas syringae* pv. *tabaci* 6605	Trypsin, TOF (DHB, sinapinic), glycopeptides	Virulence affected by glycosylation. Trisaccharide attached to serine	(Taguchi et al., 2010)
Ghrelin-like glycopeptide from *Dasyatis akajei* (red stingray) stomach	*O*-glycanase, TOF (CHCA), glycopeptides	Structural determination. $HexNAc_3Hex_2$ at Thr-11	(Kaiya et al., 2009)
β-D-Glucans from laminaran	TOF, glycans	Effect on formation of germs of buckwheat	(Fedorova et al., 2010b)
Glyceraldehyde-3-phosphate dehydrogenase from rat	β-elimination and Michael addition (BEMAD), TOF/TOF, glycopeptides	O-GlcNAc disrupts target protein homo-tetramer formation and mediates its nuclear translocation	(Park et al., 2009b)
Grass pollen group 1 allergens	TOF (CHCA, DHB), ESI, glycopeptides	Structural determination, $Pentose_{(1-3)}$	(Fenaille, et al., 2009)
HOC 89 and ovarian cyst 19 glycoproteins	β-Elimination, MALDI, MS/MS, glycans (per-Me)	Determination of the location of A and B blood groups on *O*-glycans	(Yu et al., 2009b)
MUC1 from human urine	β-Elimination (ammonium carbamate), R-TOF/TOF (DHB), glycans, MS/MS	Development of release method using glycoblotting and NH_4 carbamate for β-elimination (Core 1, core 2 glycans)	(Miura, et al., 2010b)
Notch epidermal growth factor (mouse in CHO cells)	Trypsin, TOF (CHCA), glycopeptides	Identification of Xyl-transferases that glycosylate *O*-Glc	(Sethi et al., 2010)

(*Continued*)

TABLE 12. (*Continued*)

Notch receptors from *Kluyveromyces lactis* expression system	Trypsin, L-, R-TOF/TOF (CHCA), glycopeptides	Methods for detection of *O*-GlcNAc modifications	(Sakaidani et al., 2010)
Oligomeric xylans from corn fibre	Alkali, TOF (DHB), glycans	Characterization of oligomeric xylans resistant to mild acid pretreatment	(Appeldoorn et al., 2010)
Osteopontin from human milk	β-Elimination (NH_4 carbamate), R-TOF/TOF (DHB), glycans (BOA derivs), MS/MS	Development of release method using glycoblotting and ammonium carbamate for β-elimination	(Miura, et al., 2010b)
Pilin from *Synechocystis* sp. PCC 6803 (cyanobacterium)	Trypsin, TOF/TOF (CHCA), glycopeptides	Alteration in *O*-glycans is responsible for the loss of pilus-mediated motility	(Kim et al., 2009g)
Proline-rich proteins from human saliva	TOF/TOF, glycoproteins	Identification of new post-translational modifications	(Vitorino, et al., 2010)
Protein C inhibitor from human blood	Trypsin, TOF, glycopeptides	Determination of *O*-linked site by methylamine release	(Sun, et al., 2010b)
PTTTPITTTTK peptide (synthetic)	TOF	GalNAc-transferase 3 involved in transfer of GalNAc in colon cells	(Kato et al., 2010a)
Skp1 from *Dictyostelium*	TOF (sinapinic)	Skp1 shown to be involved in O_2 regulation of development	(Wang et al., 2009k)
Synthetic, from mucin glycopeptides	R-TOF (DHB, 2-OH-benzoic acid), ESI, glycopeptides	Influence of protein and glycans on nearby residues on four glycosyl-transferases assembling the extended core 2 structure	(Brockhausen et al., 2009)
Synthetic (MUC1 repeat decapeptide)	R-TOF, glycopeptides	Identification of *O*-glycosylated decapeptides within the MUC1 repeat domain as potential MHC class I (A2) binding epitopes	(Ninkovic et al., 2009)
Vitamin D binding protein, Gc globulin from human plasma	Trypsin, Q-TOF (DHB), glycoprotein	Structural determination. GlcNAc-Gal-Neu5Ac at Thr 420	(Ravnsborg et al., 2010b)
von Willebrand factor from human plasma	β-elimination, TOF/TOF (DHB), glycans (per-Me), GC/MS	Structural determination (Core 1, core 2)	(Canis et al., 2010)

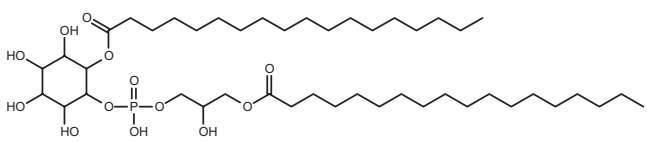
[1]Format (not all items present): Glycan release method and/or protease, MALDI method (matrix), compounds run (derivative), other methods.

allowed the molecular ion to be detected in nearly all cases and gave fragments arising from the loss of sulfate groups. *Nor*-harmane, in contrast, produced mainly fragments. In all cases, ions retaining the sulfate groups were observed making these fragments essential for assigning the sulfated positions of each residue. While *nor*-harmane was not able to produce enough analyte desorption/ionization, fragments useful for structural assignment were produced by the addition of butylammonium formate to the DHB matrix.

5. *Glycosyl-phosphatidylinositol (GPI) Anchors*

A method for analysis of GPI anchors on the "proteomic" scale has been described (Mehlert & Ferguson, 2009). Partially purified proteins were separated by SDS–PAGE and then blotted onto a PVDF membrane. Following identification of the protein, the GPI anchor was analyzed by three methods. First, the compound was hydrolyzed with HCl in the presence of [1,2,3,4,5,6-$^2H_6$]-myo-inositol and the hydrolysate was analyzed as trimethylsilyl (TMS) derivatives by GC/MS. Next, the phosphate bonds were cleaved and the carbohydrate structure was elucidated by electrospray or MALDI-TOF MS. Finally, the diacylglycerol-attached myo-inositol moiety was detached by nitrous acid deamination and analyzed by negative ion electrospray.

Bütikofer et al. (2010) have studied lipid remodeling of GPI glycoconjugates in procyclic-form trypanosomes and shown that, in *Trypanosoma congolense*, the steady-state lipids consist of lyso-(acyl)phosphatidylinositol (PI, **66**), deacyl-PI and deacyl-(acyl)PI species, where (acyl) indicates an acyl group attached to the inositol moiety. MALDI-QIT-TOF in negative ion mode from THAP was used to analyze the PI species after deamination with nitrous acid.



Lyso-(acyl) phosphatidylinositol, **66**

TABLE 13. Use of MALDI MS for Examination of *O*-Glycans From Intact Organisms or Tissues

Organism	Methods[1]	Notes	Reference
Caenorhabditis elegans bus-2 mutant (extracts)	β-Elimination, R-TOF (DHB), GC/MS, ESI-MS/MS	Ident. of highly fucosylated novel glycans containing internally linked GlcA.	(Palaima et al., 2010)
Chinese hamster cells	β-Elimination, TOF/TOF (DHB), glycans (per-Me)	MABs bind glycans with Neu5Ac but not Neu5Gc. E-, P- and L-selectins bind both	(Mitoma et al., 2009)
Chinese hamster (glycoproteins from Lec15.Lec1 mutants)	β-Elimination, R-TOF, TOF/TOF (DHB, arabinosazone), glycans (per-Me)	To investigate action of glycoprotein Large	(Aguilan, et al., 2009)
Chinese hamster mutants (cellular glycoproteins)	β-Elimination, TOF, TOF/TOF (DHB), glycans (per-Me), GC/MS	Structural determination of glycans from Lec1, 2, 3.2.8.1, 4, 10, 11, 12, 13, and 30 mutants	(North, et al., 2010a)
Danio rerio (Zebrafish embryos)	β-Elimination, R-TOF/TOF (DHB), glycans (per-Me)	Developmental regulation of oligo-sialylation	(Chang, et al., 2009)
Echinococcus granulosus (cestoid larva), (surface glycans)	β-Elimination, TOF/TOF (CHCA), glycans (per-Me)	Structural determination. Core 1 and 2 capped with novel Gal*p*-α (1→4) group	(Díaz et al., 2009)
Human neutrophils	β-Elimination, TOF, TOF/TOF (DHB) glycans (per-Me)	Structural determination (Core 1, core 2). Samples from geographically remote labs. Similar glycans	(Babu, et al., 2009)
Human, (enterocyte-like HT-29 cells)	β-Elimination, TOF, glycans (per-Me), GC/MS	Structural determination (Core 1)	(Morelle, et al., 2009b)
Human (mesenchymal stem cells from bone marrow)	Non-reductive β-elimination, R-TOF/TOF, FT-ICR (DHB), glycans (per-Me)	Structural determination. (Core I, Core 2). Can be used to evaluate cellular differentiation stage	(Heiskanen, et al., 2009)
Human seminal plasma	β-Elimination, TOF/TOF (DHB), glycans (per-Me)	Structural determination (Core I, core 2). Poly-fucosylation	(Pang, et al., 2009)
Human (Caco-2 colon carcinoma cells)	β-Elimination TOF/TOF, glycans (per-Me)	Core2 *O*-glycan essential for cell surface expression	(Lee et al., 2010c)
Human serum	β-Elimination (NH_4 carbamate), R-TOF/TOF (DHB), glycans, MS/MS	New release method: glycoblotting and NH_4 carbamate for β-elimination, sialyl-T and disialyl-T antigens	(Miura, et al., 2010b)
Human (cytolytic T lymphocytes)	β-Elimination, TOF/TOF (DHB), glycans (per-Me)	Loss of effector function shown to be accompanied by major changes in *N*- and *O*-glycosylation	(Antonopoulos, et al., 2012)
Leishmania sp. (sialic acids from promastigotes)	HAc, TOF (DHB), GC/MS, Neu5Ac, Neu5Gc, 7-*O*-Ac-Neu5Ac, 8-O-Ac-Neu5Ac, 9-*O*-Ac-Neu5Ac	Identification of sialic acids in different species and correlation with nitric oxide resistance	(Ghoshal et al., 2010)
Mouse (various tissues)	β-Elimination, TOF/TOF (DHB), glycans (per-Me)	Study of GalNAc transferases in production and function of Core 2 glycans	(Stone, et al., 2009)
Mouse (intestinal mucus)	β-Elimination (NH_3 based), L-TOF (DHB), glycans (2-AB)	Core 3-derived glycans shown to be essential for intestinal mucus barrier function.	(Xia, 2010)
Mouse (Fut-2 null) from gastric mucosa	β-Elimination, TOF/TOF (DHB), glycans (Per-Me)	Absence of fucose on Core 3 glycans impairs BabA-mediated adhesion to gastric mucosa	(Magalhães et al., 2009)

(*Continued*)

TABLE 13. (*Continued*)

Ox submaxillary mucin	β-Elimination (ammonium carbamate), R-TOF/TOF (DHB), glycans ((BOA(F)), MS/MS	Development of release method using glycoblotting and ammonium carbamate for β-elimination	(Miura, et al., 2010b)
Pig gastric mucin	TOF/TOF (DHB), glycans (Per-Me)	Mucin-lectin interactions assessed by flow cytometry	(Jeffers et al., 2010)
Rat gastric mucin	Hydrazine, TOF (DHB), glycans (2-AA)	Structural determination and evaluation of hydrazine-release method	(Goso, et al., 2009)
Rhesus monkey infected with *Helicobacter pylori* (gastric mucin)	β-Elimination, FT-ICR (DHB), glycans	*H. pylori*-induced gastritis accompanied by acute and dramatic decrease in diversity and abundance of *O*-glycans. Recovered over 24-weeks	(Cooke et al., 2009)

[1]Format (not all items present): Glycan release method and/or protease, MALDI method (matrix), compounds run (derivative), other methods.

6. S-Layer Glycoproteins

Although many bacteria produce S-layer proteins with glycosylation, Qazi et al. (2009) have used MALDI-TOF MS to show that those from *Clostridium difficile* are not glycosylated.

7. Glycated Proteins (Non-Enzymatic Attachment of Sugars)

This topic has been reviewed by Zhang et al. (2009f) and Capote and Sanchez (2009). MALDI is used mainly to determine the extent of glycation of intact proteins or to determine the sites of attachment of the covalent glycans.

a. Specific methods for glycated peptides

Amadori peptides have been enriched with boronate affinity tips for measurement by MALDI-TOF/MS. The tips showed the highest binding efficiency for glucose at pH 8.2 employing ammonium chloride/ammonia buffer with ionic strength of 150 mM. The bound constituents were released by sorbitol (**1/42**) or formic acid. Using sorbitol for elution required desalting prior to analysis. Of three different sorbents tested: fullerene-derivatized silica, ZipTips (C18), and C18 silica, fullerene-derivatized silica and ZipTips showed the same performance with respect to the numbers of glycated peptides and gave better performance than C18 silica. Fewer glycated peptides were detected by LC-MS/MS than by MALDI (Takátsy et al., 2009).

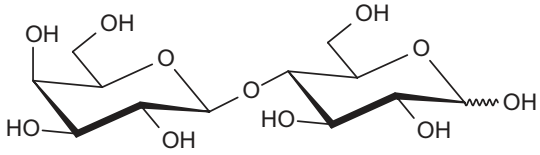
A novel fullerene(C60)-derivatized silica material has been compared with octadecyl(C18) and triaconthyl(C30)-silicas for their ability to recover peptides from digests of HSA and fibrinogen. C30- and particularly the C60(30 nm)-SPE materials were found to be the two most effective. After glycation the digests of fibrinogen and HSA were also separated. This new method made the detection of a considerably higher number of glycated peptides possible compared to the unfractionated digests and the use of boronate affinity chromatography in the case of fibrinogen. For HSA, 10 new sites of glycation at Lys and Arg residues were found (Böddi et al., 2009).

A mass spectrometric method for screening large tandem mass spectrometric (MS/MS) datasets for protein glycation with glucose (**1/4**), lactose (**67**) and maltose (**68**) has been developed (Montgomery, Tanaka, & Belgacem, 2010). Control experiments using a standard peptide containing a single glycation site led to the discovery of characteristic neutral loss fragmentation patterns in MS/MS analysis for glucose, lactose and maltose condensed with peptide. For glucose glycation, neutral losses of 36, 120, and 162 Da were observed in accordance with previously published reports. The neutral loss patterns for lactose and maltose were found to be identical, with characteristic losses of 162, 198, 282, and 324 Da. These signature losses were observed irrespective of the MALDI mass spectrometer used and were valid in both TOF–TOF and QIT–TOF instruments. These neutral loss signatures were then applied to elucidation of modified peptides from a complex HSA digest glycated with each of the proposed sugars. Screening of these large datasets

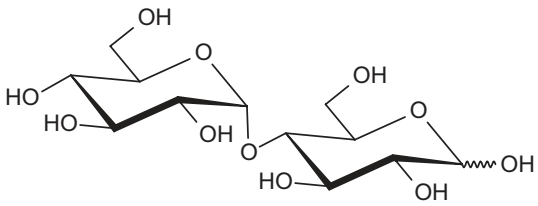
TABLE 14. Reviews and General Articles on the Analysis of Glycosaminoglycans (GAGs)

Subject	Comments	Citations	Reference
Advances in the separation, sensitive detection, and characterization of heparin and heparan sulfate	Sections on MALDI and ESI MS	77	(Korir & Larive, 2009)
Details for structural elucidation of GAGs	Practical details	26	(Prabhakar et al., 2009)
Glycomics profiling of heparin sulfate structure and activity	Methods for isolation and profiling	68	(Turnbull et al., 2010)
On-line separations combined with MS for analysis of GAGs	Includes FAB, MALDI and ESI MS	167	(Zaia, 2009)

was made possible by specifically designed software that enabled the input of detailed user-defined post-translational modifications that are not included in the universally available databases such as Unimod.



Lactose, **67**

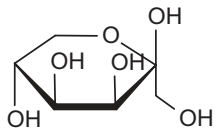


Maltose, **68**

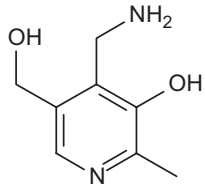
A quantitative method for measuring glycation sites on HSA has been reported (Barnaby et al., 2010). A sample containing *in vitro* glycated HSA was digested with various proteolytic enzymes in ^{18}O-enriched water and, in parallel, a normal HSA sample, with no significant levels of glycation, was digested in unlabeled water. The samples were mixed and the $^{16}O/^{18}O$ ratios of the peptides were measured in each digest by MALDI-TOF MS. The values obtained for the $^{16}O/^{18}O$ ratios were used to determine the degree of modification that had occurred in various regions of glycated HSA. Peptides containing Args 114, 81, or 218 and Lyss 413, 432, 159, 212, or 323 were found to have $^{16}O/^{18}O$ ratios greater than a cut off value of 2.0. A qualitative comparison of the ^{16}O- and ^{18}O-labeled digests indicated that Lyss 525 and 439 also had significant degrees of modification. The modifications that occurred at these sites were variations of fructosyl-Lys and advanced glycation end products (AGEs) which included 1-alkyl-2-formyl-3,4-glycoyl-pyrole (**4/45**) and pyrraline (**4/44**).

The fragmentation behavior of the peptide Ac-PAAPAA-PAPAEKTPV-OH (human histone H1.4, positions 6–20) glycated *via* its Lys residues to ADP-ribose has been studied by Fedorova, Frolov, and Hoffmann (2010a). Under MALDI conditions, the ADP-ribosyl group was cleaved, almost completely at the pyrophosphate bond by ISD and PSD. However, this cleavage was very weak in ESI-MS. The remaining phospho-ribosyl group was stable, providing a direct and reliable identification of the glycation site *via* the b- and y-ion series.

As well as being associated with health problems, in for example, diabetes, protein glycation is important in the food industry in, for example, the browning of food during cooking. The reaction is also being used to attach carbohydrates to proteins to improve technological and biological functionalities. In relation to this latter use, Corzo-Martnez et al. (2010) have used MALDI-TOF MS to study the reaction between β-lactoglobulin and the sugars galactose and tagatose (**69**) and found that the reaction can be competitively moderated with pyridoxamine (**70**).



Tagatose, **69**

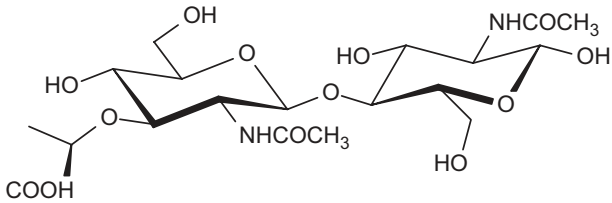


Pyridoxamine, **70**

Other reports of the use of MALDI to study glycation of specific proteins are summarized in Table 15.

F. Peptidoglycans

Typical structures consist of GlcNAc-MurNAc (**71**) disaccharides cross-linked by short peptides. They are usually analyzed as muropeptides following enzymatic digestion. Reports of the use of MALDI to study peptidoglycans and muropeptides are summarized in Table 16.



71

G. Glycolipids

This is a very large group of compounds but most work involving MALDI has been concentrated on the LPS from bacteria and the GSLs. Work, mainly involving structural determination, on the many other types of glycolipids found in bacteria and similar organisms, is summarized in Table 17. A general review on analysis of microbial glycopolymers has been published by Brandenburg, Garidel, and Gutsmann (2009), and Fuchs and Schiller (2009) have discussed applications of MALDI-TOF MS to lipidomics. A more general review by Fuchs, Süß, and Schiller (2010) covers applications of MALDI-TOF MS coupled to TLC and includes applications to glycolipids and carbohydrates.

1. Lipopolysaccharides (LPS)

These compounds form the outer membranes of gram-negative bacteria and consist of the anchoring lipid A (**1/18**) composed of two glucosamine (GlcN) residues linked to several long-chain fatty acids, a core carbohydrate region and often a very long carbohydrate, the O-chain, composed of repeating oligosaccharide units. Extraction is usually with solvent mixtures such as

TABLE 15. Use of MALDI MS for the Investigation of Glycated Proteins

Protein/amino acid	Sugar	Methods[1]	Notes	Reference
Albumin (human serum)	Glucose	TOF (DHB, CHCA)	Development of a quantitative analysis of glycation sites	(Barnaby, et al., 2010)
Barley proteins	Glucose	Chymotrypsin, TOF/TOF (CHCA)	Detection of glycation sites	(Petry-Podgórska et al., 2010)
Casein	Glucose	TOF (sinapinic)	Use of FT-IR, ESI and MALDI-TOF to characterize glycated caseins	(Oliver et al., 2009)
Human serum albumin (HAS)	All, Glc, Fru, Psi	TOF	Glycation by allose greater than that by glucose	(Kajikawa et al., 2010)
Insulin	D-Glucose	R-TOF/TOF (sinapinic, CHCA)	Glycation sites characterized for first time (Gly-1 and Phe-1 of both chains, Lys-29 of B-chain)	(Guedes et al., 2009)
Insulin	Glucose	R-TOF/TOF (CHCA)	Study of oxidative modifications in glycated insulin, Tyr, Phe and Cys were main affected residues.	(Guedes et al., 2010)
Insulin	Glucose	TOF	Development of assay for screening glycation inhibitors. Rifampicin new antiglycating compound	(Golegaonkar et al., 2010)
α-Lactalbumin	Lactose	TOF	Fast and reliable method to monitor early Maillard reaction during milk processing	(Meltretter et al., 2009)
β-Lactoglobulin	Glucose, lactose	R-TOF (CHCA)	Effect of glycation on foam and structural properties	(Medrano et al., 2009)
β-Lactoglobulin	Galactose, tagatose	TOF (sinapinic)	Identification of glycated protein in study mainly by LC-MS/MS	(Corzo-Martínez et al., 2009)
β-Lactoglobulin	Galactose, tagatose, dextran	TOF (sinapinic)	Effect of glycation on gastrointestinal digestibility and immunoreactivity	(Corzo-Martínez et al., 2010)
Large proteins (HSA, BSA, IgG)	Glucose	L-TOF	Larger proteins shown to acquire more carbohydrate molecules than small ones.	(Bhonsle & Kulkarni, 2009)
Lysozyme	Glucose	TOF, NMR	First products observed after three hours. Nine D-glucose units are attached during ten weeks at 37°C.	(Maekawa et al., 2010)
Lysozyme, EPK177, physalaemin	Glucose, dextran 1000, maltotriose, maltopentaose	TOF (s-DHB, CHCA, sinapinic, DHAP) ESI	Investigation of the formation of high-molecular-weight coloured compounds, called melanoidins, in food	(Smaniotto et al., 2009)
Porcine serum albumin (PSA)	Lactose	TOF (CHCA)	To produce prophylaxis of piglet diarrhea	(Sarabia-Sainz et al., 2009)
Protein Z from barley	D-glucose	R-TOF (CHCA)	Use of protein Z glycation to monitor malting in beer production	(Bobálová et al., 2010)
Proteins from milk	Lactose	Trypsin, TOF (DHB), glycopeptides	Study of lactosylation of proteins under various technological procedures	(Arena et al., 2011)
Water-soluble proteins	Glucose	L-TOF (2,6-DHAP)	Use of MALDI-TOF to study glycation during malting	(Laštovičková et al., 2010)

[1]Format (not all items present): MALDI method (matrix), compounds run (derivative), other methods.

phenol/chloroform/petroleum ether and the molecules are frequently split into their component parts by mild acid hydrolysis for further structural analysis. Dephosphorylation and deacylation are also common. Reviews on the structural investigation of bacterial LPS by MS and MS/MS have been published by Banoub et al. (2010) and by Grice and Wilson (2009). Lipid A from *Coxiella burnetii*, the causative agent of Q fever has been discussed by Toman, Skultety, and Ihnatko (2009) and a more general review of the core region and lipid A of LPS has been published by Holst and Molinaro (2010).

a. Intact LPS

The first structures of LPS to be elucidated from cyanobacteria has been reported by Snyder et al. (2009). Two strains of marine

TABLE 16. Use of MALDI MS for Examination of Bacterial Peptidoglycans and Muropeptides

Species	Peptidoglycan	Methods[1]	Notes	Reference
Bacillus anthracis	Peptidoglycan of capsule	TOF (CHCA)	Capsule anchoring shown to occur by a transpeptidation reaction. Inhibited by capsidin	(Richter et al., 2009)
Bacillus megaterium QM B1551	Muropeptides	TOF (DHB)	To study mutational properties of cortex-lytic enzymes	(Christie et al., 2010)
Bacillus subtilis	MurNAc-tetrapeptide	TOF (CHCA)	Muropeptide rescue shown to involve sequential hydrolysis by β-GlcNAc-ase and *N*-acetyl-muramyl-L-alanine amidase	(Litzinger et al., 2010)
Escherichia coli	Peptidoglycans	TOF	Study of the action of peptidoglycan hydrolyses	(Uehara et al., 2010)
Helicobacter pylori	Peptidoglycans	TOF (DHB)	Identification of oxidative stress-induced peptidoglycan deacetylase	(Wang et al., 2009d)
Helicobacter pylori	Muropeptides and anhydro-muropeptides	TOF	Study of the involvement of a peptidoglycan-modifying enzyme in regulating the shape of the bacterium	(Bonis et al., 2010)
Lactococcus lactis	Muropeptides	TOF (CHCA)	Peptoglycan synthesis altered when *L. plantarum* genes substituted. Increased vancomycin resistance	(Deghorain et al., 2010)
Mesorhizobium loti HAMBI 1148	Muramyl residues from cell wall	L-TOF (DHB)	Localization of the attachment site of oligoglucans to murein	(Karas & Russa, 2009)
Mycobacterium avium	Glyco-peptidolipid	TOF/TOF (DHB), GC/MS	Novel rhamnosyltransferase involved in biosynthesis	(Miyamoto et al., 2010)
Salmonella typhi	Muropeptides	TOF	Three muropeptides isolated and effects on dendritic cells studied	(Pashenkov et al., 2010)
Shark	Hexasaccharide-peptide from cartilage proteoglycan	L-TOF (DHB)	Development of a mouse monoclonal antibody against the chondroitin sulfate-protein linkage region	(Akatsu et al., 2010)
Thermotoga maritima	Muropeptides from peptidoglycan	R-TOF (DHB), ESI-MS/MS	Structure elucidation and identification of two novel types of cross-link	(Boniface et al., 2009)

[1]Format (not all items present): MALDI method (matrix).

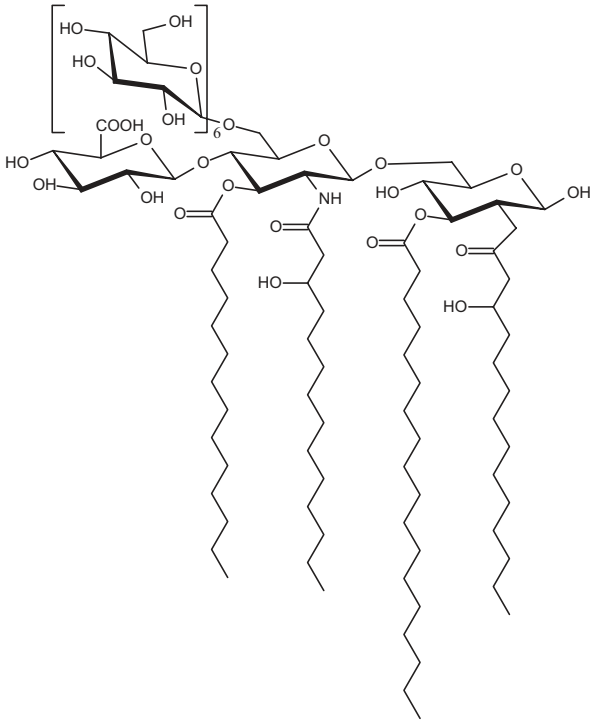
Synechococcus, WH8102 and CC9311, were used and were shown to have very simple structures without the complex O-chain found in most proteobacteria. The LPS (**72**) of these cyanobacteria did not contain phosphate, heptose (Hep) or Kdo (**1/13**) but instead possessed 4-linked glucose as their main saccharide component, with low levels of GlcN and galacturonic acid (GalA). MALDI-TOF MS of the intact minimal core LPS revealed triacylated and tetraacylated structures with a heterogeneous mixture of both hydroxylated and nonhydroxylated fatty acids connected to the di-GlcN backbone. In contrast to enteric lipid A, which can be liberated from LPS by mild acid hydrolysis, lipid A from these organisms could be produced only by two novel procedures: triethylamine-assisted periodate oxidation and acetolysis.

Unique caryophyllose (α-3,6-dideoxy-4-*C*-(D-*altro*-1,3,4,5-tetrahydroxyhexyl)-D-*xylo*-hexopyranose, **73**)-containing cell wall glycolipids have been identified in LPS from *Mycobacterium marinum* (Rombouts et al., 2009). MALDI-TOF spectra were obtained from DHB and ESI-MS/MS was used to elucidate the glycan sequence.

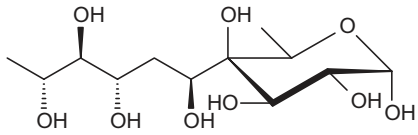
b. Lipid A

Sample preparation has been shown to be critical for assessing the true composition of these compounds. In a comparative study, Kawasaki (2009) have shown that MALDI-TOF MS analysis of lipid A prepared using a commercial "Tri-reagent"-based procedure with a 5-chloro-2-mercaptobenzothiazole (CMBT) (**1/33**) matrix gave the best results for compounds with a phosphoethanolamine (PEt*N*) modification. In contrast, the analysis of lipid A prepared using an LPS extraction kit-based procedure with DHB was preferable for the detection of an aminoarabinose modification.

For isolation of lipid A from *Yersinia enterocolitica*, Pérez-Gutiérrez et al. (2010) used an ammonium hydroxide-isobutyric acid method. Lyophilized crude cells were incubated with isobutyric acid and ammonium hydroxide (5:3, v/v) at 100°C for 2 hr, washed twice with methanol and the insoluble lipid A was solubilized in chloroform–methanol–water (3:1.5:0.25, v/v/v). Analysis was by MALDI-TOF MS from DHB in negative ion mode because of the presence of two phosphate groups. The lipid as A contained both four or six fatty acyl chains whose



LPS from *Synechococcus* spp., **72**



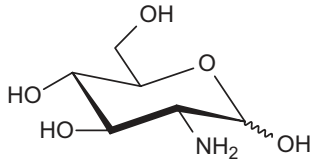
α-3,6-Dideoxy-4-*C*-(D-*altro*-1,3,4,5-tetrahydroxyhexyl)
-D-*xylo*-hexopyranose, **73**

ratio changed with growth temperature. A similar method has been used by March et al. (2010) to study lipid A from *Acinetobacter baumannii*. The molecules were found to have from four to seven acyl groups.

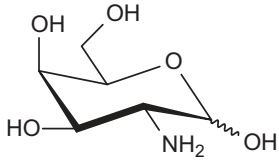
A microwave-assisted method for obtaining Lipid A from *Helicobacter pylori* has been developed by Zhou et al. (2009a). Lyophilized cells were suspended in sodium acetate buffer (pH 4.5) containing proteinase K and subjected to microwave irritation at 50 W for 5 min at 58˚C and then kept for 1 hr at 100˚ C. After centrifugation and washing, the dried supernatant was examined by MALDI-TOF/TOF from CMBT. The reliability of the technique was demonstrated by analysis of the lipid A from bacterial cells of different *H. pylori* strains. The phosphorylation and acylation patterns could be elucidated using material from a single colony. Furthermore, the investigators found unusual heptaacyl lipid A species present in low abundance in *H. pylori* mutant that have not been previously reported. The study was claimed to provide the first characterization by MS of the lipid A component from a single bacterial colony.

The mass spectrometric behavior of lipid A is highly dependent on both the matrix and phosphorylation patterns. Zhou et al. (2010a) have investigated the effects of different matrices and co-matrices using lipid A from *Escherichia coli* O116 as a model system. Good results were obtained with CMBT with added EDTA (**5/43**) ammonium salt as the matrix. This matrix system was found to enhance the sensitivity of the detection of diphosphorylated lipid A by more than 100-fold and, in addition, provided tolerance to high concentrations of SDS and to both sodium and calcium chlorides at μM concentrations. The method was evaluated for analysis of lipid A with different phosphorylation patterns and from different bacteria, including *H. pylori*, *Salmonella enterica* serovar Riogrande, and *Francisella novicida*.

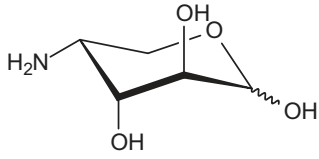
An LC/MS-based assay has been developed for the quantitation of aminosugars, including GlcN (**74**), galactosamine (GalN, **75**) and aminoarabinose (AraN, **76**) together with ethanolamine (EtN), present in lipid A and has been applied to the analysis of lipid A isolated from several biosynthetic and regulatory mutants of *S. enterica* serovar *Typhimurium* and *Francisella tularensis* subspecies *novicida* characterized by MALDI-TOF. Lipid A was treated with TFA to liberate and deacetylate individual aminosugars and mass tagged with 6-aminoquinolyl-*N*-hydroxysuccinimidyl carbamate (**77**), which reacts with primary and secondary amines. The derivatives were separated using RP-chromatography and analyzed with a quadrupole MS to detect quantities as small as 20 fmol. GalN was detected only in *Francisella* and AraN only in *Salmonella*, while GlcN was detected in lipid A samples from both species (Kalhorn et al., 2009).



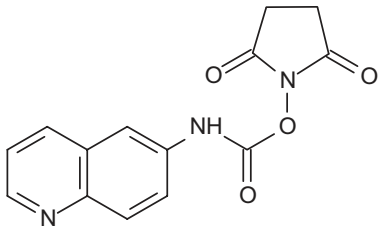
Glucosamine (GlcN), **74**



Galactosamine (GalN), **75**



Aminoarabinose (AraN), **76**



6-Aminoquinolyl-*N*-hydroxysuccinimidyl carbamate, **77**

TABLE 17. Use of MALDI MS for Examination of Bacterial Glycolipids (Lipid A-Linked)

Species	Type	Methods[1]	Notes	Reference
Acinetobacter baumannii	Lipid A	R-TOF (DHB)	In pneumonia, airway epithelial cells shown to produce mediators important for bacterial clearance	(March, et al., 2010)
Actinobacillus suis	Free deca-saccharide	TOF (DHB), NMR, glycan	Structural identification in the swine pathogen (*A. suis*)	(Deutschmann et al., 2010)
Aeromonas caviae	LPS	R-TOF (DHB), glycans (per-Me)	Identification of genetic island containing genes required for biosynthesis of Pse5Ac7Ac	(Tabei et al., 2009)
Aeromonas hydrophila (chemotype II)	Core	Q-TOF (DHB), ESI, glycans (per-Me)	Structural determination	(Sioud, et al., 2010)
Aeromonas hydrophila and A. *salmonicida*	Core	R-TOF (DHB), PSD	Bifunctional enzyme (WahA) in a single gene shown to catalyze Incorporation of GlcN into core	(Jimenez et al., 2009a)
Aeromonas salmonicida subsp. *Salmonicida* A450	Core	TOF (DHB), PSD	Genetics and proteomics of lipopolysaccharide core biosynthesis. Comparison with *Aeromonas hydrophila* AH-3	(Jimenez et al., 2009b)
Alkaliphilic *Halomonas* sp.	Core-lipid A	TOF/TOF (THAP), GC/MS, GLC, NMR	Structural determination	(Silipo et al., 2010b)
Bacillus cereus Subspecies *cytotoxis* NVH 391-98	UDP-2-acetamido-2-deoxyxylose	TOF (DHB), NMR	Identification of biosynthetic route	(Gu et al., 2010a)
Bacteroides fragilis, B. thetaiotaomicron, Porphyromonas gingivalis	Lipid A	TOF (CMBT), GLC	Structurally similar penta-acylated LPS of *P. gingivalis* and *Bacteroides* elicit strikingly different innate immune responses	(Berezow et al., 2009)
Bacteriovorax stolpii	Lipid A	TOF (DHB), ESI, GC/MS	Structural determination	(Beck et al., 2010)
Bordetella parapertussis	Lipid A	TOF (DHB), PDMS	Structural determination	(El Hamidi et al., 2009)
Burkholderia cenocepacia	LOS	L-TOF (THAP, nitrocellulose)	Structural elucidation of LOS isolated from a cystic fibrosis patient after lung transplantation	(Ieranò et al., 2010a)
Burkholderia cenocepacia K56-2	Core	L-TOF, NMR	Mutants with truncated cores lead to increased binding and sensitivity to polymyxin B	(Ortega et al., 2009)
Burkholderia rhizoxinica	LPS	MALDI, GC/MS	Structural identification of an unusual Gal-Fuc LPS that ensures survival of toxin-producing bacteria in fungal host	(Leone et al., 2010)
Burkholderia vietnamiensis	LPS	TOF (THAP), NMR	First structural ident. of *B. vietnamiensis* LPS from cystic fibrosis-associated lung transplantation strains. Changes limited to lipid A. Increased acylation post transplant.	(Ieranò et al., 2009)
Campylobacter jejuni	Lipid A	TOF	Identification of gene encoding phosphatidylethanolamine transferase	(Cullen & Trent, 2010)

(*Continued*)

TABLE 17. (*Continued*)

E. coli (D31m4 strain)	LPS	TOF (ATT)	Extraction of LPS and study of interaction with polymyxin	(Mares et al., 2009)
E. coli with genes from *Haemophilus influenzae*	LPS	TOF (DHB), GC/MS	Allowed specificity of various glycosyltransferases to be assigned to individual genes (lsgC-F)	(Johansen et al., 2010)
E. coli and *Salmonella enterica*	LPS	TOF/TOF (ATT)	Engineered to produce GM3 carbohydrate	(Ilg et al., 2010)
Francisella tularensis	Lipid A	TOF (DHB)	Structure of grey form in "blue-grey" phase contains more GlcN on phosphate	(Soni et al., 2010)
Hafnia alvei 32	LPS	TOF (THAP, ESI, NMR	Structural determination. Identification of two Kdo-heptose regions and serological screening of different *Hafnia* O serotypes	(Lukasiewicz et al., 2009)
Hafnia alvei PCM 1195	O-Specific poly-saccharide	TOF (DHB), GC/MS, NMR	Structural determination. Novel O-antigen with a teichoic acid-like structure	(Niedziela et al., 2010a)
Hafnia alvei 32 and PCM 1195	Lipid A	TOF (DHB, 9H-Pyrido[3,4-] -indole), ESI, GC/MS	Structural determination	(Lukasiewicz et al., 2010)
Halomonas alkaliantarctica strain CRSS	O-chain	TOF, NMR	Structural determination	(Pieretti et al., 2009a)
Halomonas alkaliantarctica strain CRSS	Core of LPS	TOF (DHB), PSD	Structural determination. $(\alpha\text{-L-Rha}p)_3$	(Pieretti et al., 2010a)
Helicobacter pylori	Lipid A	R-TOF (ATT)	Removal of outer Kdo shown to affect all domains of LPS	(Stead et al., 2010)
Klebsiella pneumoniae and *Proteus* sp.	Core LPS	R-TOF (DHB)	Three enzymatic steps shown to be required for GalN incorporation into core LPS	(Aquilini et al., 2010b)
Klebsiella pneumoniae	Core LPS	R-TOF (DHB)	For functional identification of common LPS biosynthesis genes in *Proteus mirabilis*	(Aquilini et al., 2010a)
Loktanella rosea	LPS	TOF (DHB)	Structural determination, unique structure	(Ieranò et al., 2010b)
Marine *Synechococcus*, WH8102 and CC9311	LPS	TOF, TOF/TOF (DHB), NMR	Structural determination. Very simple structure with none of the usual phosphate, Kdo or Hep	(Snyder, et al., 2009)
Mesorhizobium huakuii 7653R	Lipid A	TOF (THAP, listed as trihydroxy-acetone)	*BacA* gene shown to be indispensable for successful *Mesorhizobium–Astragalus* symbiosis	(Tan et al., 2009)
Mycobacterium marinum	LOS	TOF (DHB), GC/MS, ESI, NMR	Ident. of unique caryophyllose-containing cell wall glycolipids that inhibit tumor necrosis factor-α secretion in macrophages	(Rombouts, et al., 2009)
Mycobacterium marinum	LOS-IV	TOF (DHB), ESI, NMR	Structural determination. Contains unusual *N*-acylated 4-amino-4,6-dideoxy-Gal*p*	(Rombouts et al., 2010)

TABLE 17. (*Continued*)

Neisseria gonorrhoeae	Lipid A	TOF (THAP)	Phosphoethanolamine substitution on Lipid A increases resistance to human innate host defences	(Lewis et al., 2009)
Neisseria gonorrhoeae and *N. meningitidis*	LOS	TOF (THAP, nitrocellulose)	Analysis mainly by MALDI-TOF. Changes in acylation and phosphorylation correlate with induction of proinflammatory cytokines	(John et al., 2009b)
Neisseria gonorrhoeae and *N. meningitides*	LOS	L-TOF (THAP, ammonium citrate)	Phosphoryl moieties of lipid A found to play an important role in activation of both MyD88- and TRIF-dependent TLR4–MD-2 signalling pathways	(Liu et al., 2010d)
Neisseria meningitides Serogroup A	LOS	TOF (ATT), GC/MS, NMR	Genetic and structural determination	(Mistretta et al., 2010)
Neisseria meningitidis Strain 89I	LOS	TOF (THAP, CMBT), GLC, GC/MS	Natural phosphoryl and acyl variants of lipid A differentially induce tumor necrosis factor-α in human monocytes	(John et al., 2009a)
Neisseria meningitides strain M986 plus three varients	LOS	TOF, ESI, NMR	Structural determination	(Tsai et al., 2009)
Neisseria sicca	LOS	L-TOF (DHB), glycans (per-Me)	Structural determination . First report of rhamnose in *Neisseria*	(O'Connor et al., 2009)
Porphyromonas gingivalis	Lipid A	TOF	Structural determination. Contribution of bacterial LPS to periodontitis	(Jain & Darveau, 2010)
Plesiomonas shigelloides Strain 302-73 (Serotype O1)	Core	TOF (DHB), NMR	Structural determination. Analysis of acid-hydrolysed product gave D-*glycero*-D-*talo*-2-octulopyranosonic acid (Ko) residue - substitutes for Kdo).	(Pieretti et al., 2009b)
Plesiomonas shigelloides O51	O-Chain	R-TOF (THAP), ESI-MS/MS, NMR	Structural determination	(Maciejewska et al., 2009)
Plesiomonas shigelloides 302–73	Core and O-chain repeat	TOF (DHB), ESI, NMR	Structural determination	(Pieretti et al., 2010b)
Porphyromonas gingivalis	Lipid A	TOF (CMBT)	Resistance to polymyxin B shown to be determined by the lipid A 4′-phosphatase, PGN 0524	(Coats et al., 2009)
Pseudomonas aeruginosa	Whole bacteria	TOF, ESI	Bacteria grown in the presence of sialic acids incorporate these compounds	(Khatua et al., 2010)
Pseudomonas aeruginosa	D-ManNAc3NAcA (mono-saccharide)	R-TOF (3,4-DHB)	Characterization of enzymes responsible for synthesising monosaccharide	(Westman et al., 2009)
Pseudomonas aeruginosa	Lipid A	TOF	Bacterium modifies lipid A and muropeptides to lower innate immunity during cystic fibrosis lung infection	(Cigana et al., 2009)
Rhizobium leguminosarum biovar viciae 3841	Lipid A	TOF/TOF (THAP)	Mutant deficient in 27-hydroxyoctacosanoate-modified LPS shown to be impaired in desiccation tolerance, biofilm formation and motility	(Vanderlinde et al., 2009)
Salmonella enterica	LPS	TOF	Use of grazing-incidence X-ray scattering and Monte Carlo simulation to investigate physics of bacterial survival against cationic antimicrobial peptides.	(Oliveira et al., 2009)

(*Continued*)

TABLE 17. (*Continued*)

Salmonella enterica serotype Typhimurium	Lipid A	TOF (CMBT)	Study on proteins (YdeI/OmdA) important for antimicrobial peptide resistance	(Pilonieta et al., 2009)
Salmonella typhimurium	Lipid A	TOF (CMBT)	3'-*O*-Deacylation shown to enhance intracellular growth within macrophages	(Kawano et al., 2010)
Shigella sonnei (WRSs2 and WRSs3)	Lipid A	TOF/TOF (CMBT, DHB)	As new, second generation vaccine candidates	(Barnoy et al., 2010)
Vibrio cholerae	Lipid A	TOF/TOF (ATT, ammonium citrate)	Secondary acylation of lipopolysaccharide requires phosphorylation of Kdo	(Hankins & Trent, 2009)
Yersinia enterocolitica	Lipid A	R-TOF (DHB)	Study of the role of acylation in virulence	(Pérez-Gutiérrez, et al., 2010)
Yersinia pestis	Lipid A deacylated LPS	R-TOF/TOF (THAP)	Phosphoglucomutase shown to be required for autoaggregation and polymyxin B resistance	(Felek et al., 2010)
Yokenella regensburgei	Core oligo-saccharide	TOF (THAP), NMR	Structural determination of two serologically nonrelated core oligosaccharides differing only by a single hexose substitution	(Niedziela et al., 2010b)

[1]Format (not all items present): MALDI method (matrix), other methods.

c. Core oligosaccharide

During an analysis of the permethylated derivative of the core oligosaccharide from *Aeromonas hydrophila*, prepared by the Hakamori method, ions appearing at 78 mass units higher than the $[M+H]^+$ ions were observed. These ions were determined to be dimethylsulfoxide (DMSO) covalent addition products resulting from the Michael addition of the dimsyl anion on the C-2–C-3 double bond of a 4,8-anhydro Kdo (**1/13**) residue followed by an addition of a proton on the double bond. Corresponding ions were also seen in methylations performed using the NaOH technique and represent the first characterization of these addition products (Sioud et al., 2010).

2. Glycosphingolipids (GSLs)

Typical pre-MALDI techniques for the analysis of these compounds include separation by TLC and cleavage of the Cer portion so that the glycan can be analyzed without the heterogeniety produced by the lipid. Reviews on the analysis of GSLs are summarised in Table 18.

a. Analysis of intact compounds

Stübiger et al. (2009) have separated lipids, including GSLs by high-performance TLC, stained them with Coomassie blue and analyzed them either directly from the TLC plates or, after their removal, with an appropriate solvent. THAP (**1/44**) was used as the matrix with acetone as the solvent for the on-plate analysis because its high volatility minimized sample spreading.

A method for structural profiling of individual GSLs in a single thin-layer chromatogram by multiple sequential immunodetection has been developed by Souady et al. (2009). Structures of the antibody-detected GSLs were determined by direct coupling of TLC with IR-MALDI after treatment of the TLC plate with glycerol. This combined technique was used to demonstrate structural GSL profiling of crude lipid extracts from human hepatocellular cancer.

A new method for analysis of GSLs involves selective ozonolysis of the C–C double bond in the ceramide moiety of biological samples and subsequent enrichment of the generated GSL aldehydes by chemical ligation using aminooxy-functionalized gold nanoparticles (aoGNP). The GSL-bound nanoparticles were removed by ultrafiltration and the GSLs were analyzed by MALDI-TOF and -TOF/TOF MS from DHB. The method was used for structural profiling of mouse brain gangliosides such as GM1, GD1a/GD1b, and GT1b for adult or GD3 in the case for the embryonic mouse. Because the saturated acyl groups remained intact, the spectra provided information on both the carbohydrate and fatty acyl moieties (Nagahori, Abe, & Nishimura, 2009).

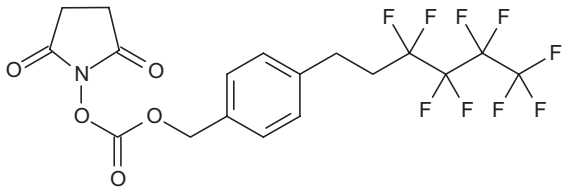
The direct structural characterization of microbial GSL receptors by use of the TLC overlay assay combined with IR-MALDI-o-TOF-MS has been described (Müsken et al., 2010). Glycan mixtures were separated by TLC in three parallel lanes. One lane was stained with orcinol and a second was overlayed with GSL-specific bacteria. The bound microbes were detected with primary antibodies against bacterial surface proteins and the relevant GSLs were detected in the third lane by IR-MALDI-TOF. The combined method worked on the microgram scale of GSL mixtures and was successfully applied to the compositional analysis of globo-series neutral GSLs recognized by P-fimbriated *E. coli* bacteria, used as model microorganisms for infection of the human urinary tract.

TABLE 18. Reviews and General Articles on the Analysis of Glycosphingolipids (GSLs)

Subject	Comments	Citations	Reference
Metabolism and analysis by new methods	Analysis mainly by MALDI	145	(Chen et al., 2010e)
MALDI-TOF directly combined with TLC.	Review of the current state	71	(Fuchs et al., 2009)
General analysis of glycosphingolipids	Covers MALDI, FAB, EI, ESI, HPLC and THC methods	280	(Haynes et al., 2009)
Direct profiling of lipids in tissues by MALDI-TOF	Covers tissue preparation and matrix selection plus applications	77	(Jackson & Woods, 2009)
Advances on the compositional analysis of glycosphingolipids combining TLC with MS	Structure and analytical methods, mainly MALDI	280	(Muthing & Distler, 2010)
Review of structural and functional analysis of GSLs from *Schistosoma mansoni*	Isolation, structural identification and interaction with receptors	78	(van Die et al., 2010)

Incubation of botulinum neurotoxin serotype D with the GSL, GT1b has produced a complex (MW 51,921) that was detected intact by MALDI-TOF MS from sinapinic acid and provided evidence that the toxin attacks neurons in a ganglioside-dependent manner (Strotmeier et al., 2010).

A method for generation of novel fluorocarbon derivatives from GSLs has been described by Li et al. (2010f). The derivatives had high affinity for fluorocarbon phases allowing them to be recovered from biological matrices by fluorous solid phase extraction (F-SPE). Sphingolipid ceramide *N*-deacylase was used to remove the fatty acid from the ceramide moiety, after which the fluorocarbon-rich substituent (F-Tag, **78**) was linked to the free amine. Finally, the molecules were permethylated for MS analysis and the method was used to examine a crude ganglioside mixture extracted from bovine brain. In addition, the flourous tag was used in a microarray format to fix F-tagged GM1 ganglioside to a fluorous glass surface, with the glycan intact and available for interaction with a fluorescent derivative of cholera toxin B chain.



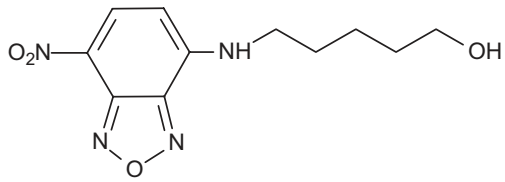
N-[4-(1H,1H,2H,2H-perfluorohexyl) benzyloxycarbonyloxyl]-succinimide, **78**

Cheng et al. (2010a) have used 9-AA (**6/18**) as a matrix for quantitative analysis of sulfatides in biological samples. The matrix was said to promote selective ionization of sulfatides in negative ion mode with a detection limit in the high attomole range. Experimental details have been published for high-performance TLC separation of glycolipids followed by blotting to a PVDF membrane in a technique termed Far-Eastern blot with analysis by MALDI-TOF MS (Taki et al., 2009).

b. Studies on the glycan moiety following removal of the ceramide

For studies of the carbohydrate portion of these molecules, lipid heterogeniety is frequently reduced by removing the ceramide with enzymes such as *Rhodococcal* endoglycoceramidase or leech ceramide glycanase. Li et al. (2009e) have described the preparation of the intact oligosaccharides from GM1 ($NeuAcGgOse_4Cer$) and $GbOse_4Cer$ as examples to show the use of ceramide glycanase and have optimized the specificity and detergent requirements of *Rhodococcal* endoglycoceramidase for the release of glycan chains from various GSLs.

A novel method of detecting 6-gala series GSLs (those possessing an R-Galβ1-6Galβ1-1-Cer, group) has been reported (Ishibashi et al., 2009). The method used the specificity of endogalactosylceramidase, an enzyme that is capable of hydrolyzing 6-gala series GSLs to produce intact oligosaccharides and ceramides but which also catalyzes transglycosylation reactions. In the latter reaction, the enzyme transferred oligosaccharides from the GSLs to acceptors such as fluorescent 1-alkanols. In this application, 7-nitro-2,1,3-benzoxadiazole pentanol (NBD-pentanol, **79**) was used as an acceptor. The fluorescent products, NBD-pentanol-conjugated-6-gala oligosaccharides, were separated and detected by TLC or HPLC with a fluorescent detector and characterized by MALDI-TOF MS. The method could also be applied to glycoglycerolipids and digalactosyldiacylglycerol and was successfully applied to detect 6-gala series GSLs in the fungus, *Rhizopus oryzae* and the parasite, *Taenia crassiceps*.



7-Nitro-2,1,3-benzoxadiazole pentanol, **79**

Other applications of MALDI to the analysis of these compounds is summarised in Table 19.

3. Rhamnolipids

Rhamnolipids are glycolipids of the type **80** produced by *Pseudomonas* spp. MALDI-TOF MS approaches have been developed for high-throughput screening of naturally occurring

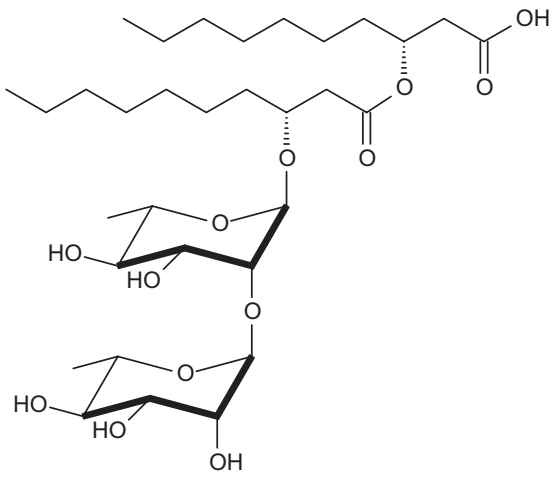
TABLE 19. Use of MALDI MS for Examination of Glycosphingolipids

Source	Methods[1]	Notes	Reference
BJAB K20 cells	TOF (THAP)	Production and use of photocrosslinking sugars to study protein:sugar interactions	(Yu et al., 2010c)
Candida albicans (Deletion mutants)	TOF (DHB)	Glucosylceramide shown to be required for virulence	(Noble et al., 2010)
Danio rerio (Zebrafish embryos)	TOF/TOF (DHB), glycans (per-Me)	Detection of oligosialylation	(Chang, et al., 2009)
Hirsutella rhossiliensis (fungus), mycelia	TOF (CHCA), PSD	Ident. of novel neogala-series glyco-sphingolipids with terminal Man and Glc	(Tani et al., 2010)
Human (mesenchymal stem cells from bone marrow)	*Macrobdella decora* endoglyco-ceramidase, R-TOF/TOF, FT-ICR (DHB), glycans (per-Me)	Structural determination	(Heiskanen, et al., 2009)
Human (colonic adenocarcinoma cell lines)	Ceramide glycanase, TOF/TOF, Q-TOF (DHB), glycans (per-Me)	Enhanced expression of β3-Gal-T 5 activity induces *in vivo* synthesis of extended type 1 chains on lactosyl-Cer	(Lin et al., 2009a)
Human (umbilical vein endothelial cells)	TOF (CHCA)	Acyl mainly 24:0. May act as biomarker for inflammation, GSL = Gb4	(Okuda et al., 2010)
Human (umbilical vein endothelial cells)	TOF (CHCA)	Structural determination and dynamics of globotetraosylceramide under TNF-α stimulation	(Okuda, et al., 2010)
Human (kidney and colon)	TOF	Identification of GSLs that bind shiga toxin from *E. coli*	(Müthing et al., 2009)
Human (embryonic stem cells)	TOF/TOF (DHB), Q-TOF (CHCA)	Switching of the core structures of GSLs from globo- and lacto- to ganglio-series on cell differentiation	(Liang et al., 2010)
Miniature pig (endothelial and islet cells)	Ceramide glycanase, R-TOF (DHB), ESI (-ve), glycans (per-Me and Girard's T)	Structural determination. Identification of Neu5Gc epitopes	(Kim, et al., 2009a) (Krambeck, et al., 2009)
Mouse (thymus)	TOF/TOF (DHB), ESI	Structural determination and natural killer T cell development	(Li et al., 2009f)
Mouse (liver and serum)	TOF (-ve)	Acute kidney injury down-regulates gene expression of hepatic cerebroside sulfotransferase. Quant. by MALDI-TOF.	(Zhang et al., 2009h)
Mouse (intestinal epithelial cells)	TOF (DHB) from TLC plate	Identification of developmental changes in GSLs (HexCer, GM3, GM1, GD1a, asialo GM1)	(Yoneshige et al., 2010)
Mouse (RAW 264.7 cells)	R-TOF, free glycans (2-AA)	To investigate GSL storage in imino sugar-treated cells	(Boomkamp et al., 2010)
Mouse (spleen/myeloma cell line)	R-TOF (DHB), GC/MS (lactotriaosylceramide analysis)	Characterization of antibodies specific to lactotriaosylceramide (from human erythrocytes	(Nozaki et al., 2010)
Mouse (synaptosomal plasma membranes)	TOF	Elevated sulfatide levels in neurones shown to cause lethal seizures	(Van Zyl et al., 2010)
Pig (olfactory epithelial membranes and cilia)	TOF (9-AA)	Use of 9-aminoacridine (9-AA) as matrix, Structural determination - phospholipids, Gal-Cer-sulfate, Gb5	(Lobasso et al., 2010)
Trichoderma viride (fungus)	L-TOF (7-NH_2-2-Me-coumarin)	Ident. of phosphocholine-containing glycosyl inositol phosphoceramides	(Uchiyama et al., 2009)

[1]Format (not all items present): Glycan cleavage, MALDI method (matrix), compounds studied (derivative) other methods.

mixtures of rhamnolipids. Mono-rhamnolipids and di-rhamnolipids were readily distinguished by characteristic molecular adduct ions, $[M+Na]^+$ and $[M-H+Na_2]^+$, with variously acylated rhamnolipids differing by 28 mu. Proton-deuterium exchange was used to confirm the number of labile hydrogen atoms and to further verify the structures. Thus, deuterated $[M+Na\text{-}^1H_4+^2H_4]^+$ and $[M+Na\text{-}^1H_6+^2H_6]^+$ ions were observed for the monorhamnolipids and dirhamnolipids,

respectively. The method was validated by compositional analysis using GC/MS, fractionation by RP-HPLC and analysis by 1 and 2D NMR (Price et al., 2009).



Rhamnolipid, **80**

4. Other Glycolipids

Applications of MALDI to the analysis of other glycolipids are listed in Table 20.

H. Glycosides

Although much work has been published on glycosides during the review period, MALDI appears to occupy a relatively minor position with fast atom bombardment (FAB) and, particularly ESI being the preferred techniques. Most work has been on the identification of glycosides from various plant sources using a variety of techniques such as nuclear magnetic resonance (NMR), UV and IR spectrometry. Applications of MALDI to the analysis of glycosides and other natural products are summarised in Table 21.

Several investigators have reported that the main fragmentation pathways of flavonoids are apparently independent of the ionization mode (ESI, atmospheric pressure chemical ionization (APCI), or MALDI) or the types of analyzers used to acquire the spectra (triQ, IT, or QTOF) as reported in a review of the structural characterization of flavonoid glycosides by multistage MS (Vukics and Guttman, 2010). MALDI-TOF (DHB) was used by Bankefors, Nord, and Kenne (2010) to examine saponins from *Quillaja saponaria* bark extracts in connection with the development of a multidimensional method using HPLC and ESI-IT MS^n for profiling complex mixtures of natural products.

XII. MEDICAL APPLICATIONS

Increasing use of MALDI has been made in the characterization and detection of disease and in the identification of biomarkers. Some of the glycan biomarkers reported for, for example, cancer, however, appear to be more associated with glycoproteins involved in inflammation and are, thus, secondary to this disease. Blomme et al. (2009) have noted that "Although individual liver diseases have their own specific markers, the same modifications, hyperfucosylation, increased branching and a bisecting GlcNAc, seem to continuously reappear in all liver diseases." Increases in fucosylated triantennary glycans from AGP is a case in point. Several reviews have appeared and are summarised in Table 22. Practical details for the characterization by MALDI-TOF and ESI-MS of *N*-linked glycosylation on recombinant glycoproteins produced in *P. pastoris* (Gong et al., 2009) and for detecting potential cancer biomarkers in various cell lines and sera from patients (An & Lebrilla, 2010) have been published.

Bereman, Williams, and Muddiman (2009a) have developed a nano-LC linear trap quadrupole (LTQ) Orbitrap method for analysis of released *N*-glycans and compared the spectra with those obtained by MALDI-FT-ICR. Whereas the MALDI spectra showed much loss of sialic acids from the sialylated glycans, the Orbitrap spectra showed no decomposition. The method was applied to glycans released from plasma glycoproteins in benign gynecologic tumors and from epithelial ovarian cancer patients. One of the biantennary glycans found to be down-regulated in the cancer patients was a fucosylated biantennary glycan in which the fucose was unusually shown attached to a Gal residue rather than to the core as determined by MS/MS. The compounds were ionized as $[M+H]^+$ species suggesting that this might be an erroneous structure and the result of an internal rearrangement that is known to occur under these conditions.

A. Cancer

A detailed statistical analysis has been performed on eight data sets of *N*-glycans released from serum glycoproteins from prostate, breast and ovarian cancer patients (Barkauskas et al., 2009) and measured by MALDI-FT-ICR MS. Significant differences between control and cancer groups were found in all eight datasets. Two structurally related compounds were found to be significantly different between control and cancer groups in all three types of cancer. These compounds had compositions of Hex_3-$HexNAc_4$-Fuc_1 and Hex_5-$HexNAc_4$-Fuc_1 and were probably from IgG rather than being produced by the cancer cells.

Narimatsu et al. (2010a) have developed a high-throughput method for detecting cancer biomarkers in early stages of the disease. Briefly, the method consisted of the extraction of tissue mRNAs and measurement of the expression by quantitative real-time polymerase chain reaction (PCR). The results suggested that different glycan structures were synthesized in different cell lines. Secreted proteins from the same cancer cells were collected from serum-free culture and then applied to a lectin microarray to select lectin(s) that showed differential binding to glycoproteins secreted from each cancer cell line. After selection of a specific lectin, isotope-coded glycosylation site-specific tagging (IGOT) was used to identify core proteins that carry an epitope bound by a specific lectin. Each candidate biomarker was immunoprecipitated from serum using commercially available antibodies and their glycan structures were profiled by lectin microarray, and finally determined by MS^n technology with measurements by MALDI-QIT-TOF MS.

Other applications are listed in Table 23.

TABLE 20. Use of MALDI MS for Examination of Glycolipids From Bacteria and Similar Organisms

Source	Glycolipid	Methods	Notes	Reference
Arcobacter halophilus	Carbohydrate backbone (pentasaccharide)	R-TOF (THAP)	α-Glc(1-7)-α-Hep-(1-5)-α-Kdo4P-(2-6)-β-GlcN4P-(1-6)-α-GlcN1P	(Silipo et al., 2010a)
Arthrobacter globiformis and *A. scleromae*	Diglycosyl glycerol	FT-ICR (DHB), NMR	Structural determination. Mannose and galactose	(Paściak et al., 2010b)
Aspergillus fumigatus	Glycoinositol-phospho-ceramides	TOF	The mitA gene shown to be required for mannosylation	(Kotz et al., 2010)
Hymenobacter sp.	Carotenoids	MALDI	Identification of 2'-methyl and 1'-xylosyl derivatives of 2'-hydroxyflexixanthin	(Klassen et al., 2009)
Leishmania major	Glycoinositol-phospholipids	TOF (CHCA), ESI-MS^n	Demonstration of a UDP-glucose independent UDP-galactose salvage pathway	(Lamerz et al., 2010)
Listeria monocytogenes	Lipoteichoic acid	TOF (DHB)	Identification of two enzyme systems involved in biosynthesis	(Webb et al., 2009)
Mycobacterium abscessus	Phosphatidyl-*myo*-inositol mannosides (PIMs)	R-TOF (HABA)	Glycopeptidolipids shown to mask PIMS in cell wall	(Rhoades et al., 2009)
Mycobacterium bovis BCG Tokyo 172 (SMP-105)	Arabinose mycolates	TOF (DHB)	Isolation and structural identification	(Uenishi et al., 2010)
Mycobacterium smegmatis	Phosphatidylinositol mannosides	TOF/TOF (DHB)	Study of biosynthesis. Ident. of essential enzymes	(Guerin et al., 2009)
Mycobacterium smegmatis	Lipo-oligosaccharides	TOF, GC/MS	Ident. of the polyketide synthase involved in the biosynthesis	(Etienne et al., 2009)
Mycobacterium smegmatis	Glycopeptido-lipids	TOF	Enzyme MmpS4 shown to promote glycopeptidolipid biosynthesis and export	(Deshayes et al., 2010)
Mycobacterium tuberculosis	Phthiocerol dimycocerosates and phenolic glycolipids	TOF/TOF	Structural determination of Beijing strain.- typical profile	(Huet et al., 2009)
Mycobacterium tuberculosis	Phthiocerol dimycocerosates	TOF	Determination the roles of FadD22, FadD26 and FadD29 in biosynthesis	(Siméone et al., 2010)
Mycobacterium tuberculosis	Phosphatidyl-*myo*-inositol mannosides	R-TOF/TOF (HABA)	Mutants used to show acyltrehalose-containing glycolipids involved in phagosome remodeling	(Brodin et al., 2010)
Mycobacterium tuberculosis	Polyprenylphospho-GalNAc (Ppg)	TOF/TOF (DHB)	Discovery of transferase Ppg for biosynthesis of arabinogalactan	(Škovierová et al., 2010)
Mycobacterium tuberculosis	Sulfoglycolipids	R-TOF (HABA)	Fatty acyl structures shown to govern T cell response	(Guiard et al., 2009)
Mycobacterium tuberculosis and *M. smegmatis*	Methylglucose lipopolysaccharides	TOF (DHB)	Study of the initiation of Me-glucose lipopolysaccharide biosynthesis	(Kaur et al., 2009)
Pseudomonas aeruginosa strain NY3	Rhamnolipids	TOF/TOF (CHCA)	Structural determination (PAH-degrading bacterium)	(Nie et al., 2010)
Rhodococcus equi	Trehalose monomycolate, trehalose dimycolate	TOF/TOF (DHB), ESI	Identification of lipids recognized by host cytotoxic T lymphocytes	(Harris et al., 2010c)

TABLE 20. (*Continued*)

Streptococcus pneumoniae (TIGR4) and *Staphylococcus aureus* (ATCC 6538)	Lipoteichoic acids (LTA)	TOF	Lipoprotein lipase and HF shown to deactivate bacterial lipoproteins and LTA. PAF-Ac-hydrolase degrades only LTAs	(Seo & Nahm, 2009)
Streptomyces coelicolor	Polyprenol phosphate Plus mannose	R-TOF/TOF (*nor*-harmane)	Investigation of glycosylation of phosphate binding protein. Man transferred from target compd.	(Wehmeier et al., 2009)
Trichomonas vaginalis	Lipophosphoglycan	TOF, FT (DHB), LC-MS	Structural determination	(Singh et al., 2009)
Various	Rhamnolipids	TOF	Isolation and characterization of rhamnolipid-producing bacterial strains from a biodiesel facility	(Rooney et al., 2009)

[1]Format (not all items present): MALDI method (matrix), compounds run (derivative), other methods.

XIII. BIOPHARMACEUTICALS

A. Therapeutic Antibodies

There is currently great interest in the production of therapeutic antibodies and MALDI-TOF MS is frequently used in the analysis of their attached glycans. Reviews have been published on methods for the production and MS analysis of IgG (Huhn et al., 2009) therapeutic antibodies (Beck et al., 2008; del Val, Kontoravdi, & Nagy, 2010; Higgins, 2010; Zhang, Pan, & Chen, 2009i) and on the humanization of recombinant glycoproteins expressed in insect cells (Tomiya, 2009). Practical details for characterization of antibody glycans have been published by several investigators (Gong et al., 2009; Janin-Bussat et al., 2010a,bJanin-Bussat et al., 2010a,b). A discussion, with experimental details, of methods based on blot detection with glycan-specific probes, MS of released glycans and LC/MS detection of glycopeptides with the aim of determining whether, how and where plant-derived biopharmaceuticals are glycosylated has also been published (Bardor et al., 2009).

Several new methods have been reported. Thus: A high-throughput method for monitoring IgG glycosylation using a 96-well plate format with IgGs purified from 2 μL of human plasma has been developed by Selman et al. (2010). IgGs were extracted using immobilized protein A, cleaved with trypsin and the resulting glycopeptides were purified by reversed-phase or hydrophilic interaction SPE. Glycopeptides were analyzed by intermediate pressure MALDI-FTICR-MS using both DHB and CHCA, both of which produced signals from sialylated as well as nonsialylated glycopeptides. The method showed an interday variation of below 10% for the six major glycoforms of both IgG1 and IgG2 and was found to be suitable for isotype-specific high throughput IgG glycosylation profiling from human plasma. The method was applied to the IgG glycosylation of 62 human samples.

Two lectin-affinity chromatography techniques, Con A and *Lens culinaris* agglutinin, have been used to enrich, by removal of high-mannose glycans, the nonfucosylated *N*-glycans from IgG with product detection by MALDI-TOF following PNGase F digestion (Tojo et al., 2009).

Prien et al. (2010) have used a stable isotopically labeled derivative for rapid glycan screening of biotherapeutics. Glycans were labeled with either [$^{12}C_6$]- or $^{13}C_6$]-2-AA for both MALDI-TOF or LC-MS analysis. The 2-AA label provided high sensitivity detection in negative ion mode and the mass separation of six units between the isotopically labeled variants eliminated problems arising from isotopic overlap.

B. PEGylated Glycoproteins

PEGylation of proteins is frequently used to prolong the serum half-life time of recombinant proteins but their very high MWs put many of them outside the mass range of commercial MALDI-TOF systems using conventional secondary electron multiplier (SEM) detectors. Seyfried et al. (2010) have investigated the use of a high mass (HM) detector combined with a MALDI linear TOF MS system for the detection of PEGylated (glyco)proteins in the range of 60–600 kDa. The system consisted of a Shimadzu AXIMA CFR+ instrument equipped with both a conventional detector and additionally, with an inline moveable HM ion conversion detector (ICD HM1, from CovalX). Spectra were run from sinapinic acid in the linear positive ion mode and were obtained from small (interferon α2a), middle (HSA) and high (coagulation factor VIII and von Willebrand factor (vWF), both heavily glycosylated proteins) molecular mass proteins. The particular challenge was the heterogeneity of the (glyco)proteins in the high MW range in combination with heterogeneity added by the PEGylation, Nevertheless, the performance of MALDI linear TOF MS was found to be superior to that of other methods. Although the SEM was able to obtain information about protein PEGylation in the mass range up to 100 kDa (e.g., PEGylated HSA), the HM system was crucial for detection of ions from the larger compounds, the masses of which sometimes exceeded 0.5 MDa. Detection of these compounds was impossible with the standard SEM. The particular challenge for the analysis was the heterogeneity of the (glyco)proteins in the high MW range in combination with additional PEGylation, which even introduced more heterogeneity and was more challenging for interpretation. Nevertheless, the performance of MALDI linear TOF MS with both detector systems in terms MW and heterogeneity determination depending on the *m/z* range was superior to the other methods.

TABLE 21. Use of MALDI Mass Spectrometry for the Study of Natural Products

Source	Compound	Instrument	Notes	Reference
Carbohydrates				
Acidiplasma aeolicum (archaeon, no cell wall)	Glyco- and phosphoglyco-lipids	TOF/TOF (CHCA)	Proposed as a member of a new genus and species	(Golyshina et al., 2009)
Aplysia kurodai (sea hare)	Glycosaminoglycans	TOF, MS/MS	Structural determination	(Yoon et al., 2010a)
Arthrobacter crystallopoietes N-08	α1,α1-trehalose	TOF, ESI, NMR	First report that trehalose can be produced from maltose in this bacterium	(Bae et al., 2009)
Beverage from fermented plant	Fructopyranose oligosaccharides	TOF, DHB	Structural determination. four compounds	(Okada et al., 2010a)
Beverage from plant extracts	Trisaccharides	TOF (DHB, GC/MS, NMR	Structural determination	(Okada et al., 2009a)
Beverage from fermented plant extracts	Trisaccharides (β-D-Glc*p*-(1-1)-β-D-Fru*f* (2-1)-α-D-Glc*p*; β-D-Gal*p*-(1-1)-β-D-Fru*f*-(2-1)-α-D-Glc*p*)	TOF (DHB), GC, GC/MS, NMR, HPAEC	Structural determination of per-methylated glycans	(Kawazoe et al., 2008)
Cryptococcus neoformans	α1,α1-Trehalose	TOF	Produced during cell wall thickening as a rescue mechanism	(Farkaš et al., 2009)
Halophila stipulacea	Malonylated glucopyranosyl flavone	MALDI	First finding of malonylated derivatives in marine phanerogams	(Bitam et al., 2010)
Lactobacillus plantarum MTCC 9510	Exopolysaccharide	TOF (dithranol)	Optimization of production methods	(Ismail & Nampoothiri, 2010)
Linum grandiflorum	Luteolin, 7-*O*-*α*-D-(6'''-E-feruloyl)-Glc*p*- (1-2)-β-D-Glc*p* and 2-[(3`-Pr^{i}-*O*-β-D-Glc*p*)oxy]-2-Me-butane nitrile	TOF	Characterization of these new compounds plus several known compounds. Cytotoxic activity against leukemia cells	(Mohammed et al., 2010)
Morinda officinalis	Polysaccharides	TOF/TOF, GC/MS, NMR	Partial structure and anti-fatigue activity	(Zhang et al., 2009a)
Morus alba (white mulberry)	Glycosylated stilbene, mulberroside A	TOF	Shows inhibitory activity against mushroom tyrosinase	(Kim et al., 2010c)
Nodularia isolate (LEGE 06071)	Glycolipids	TOF	Morphological, toxicological and molecular characterization	(Lopes et al., 2010b)
Pseudomonas syringae	β-1,2-Glucans	TOF, ESI, NMR	For chiral separation of hesperetin and hesperetin-*O*-glycoside by CE	(Cho et al., 2009c)
Pseudozyma antarctica	Biosurfactants MEL-A and MEL-B	TOF, GC/MS	To study photooxidative mineralization	(Ito et al., 2010b)
Pseudozyma hubeiensis SY62	Mannosyl erythritol lipids (MELs)	TOF (CHCA)	Biosurfactant from yeast isolated from *Calyptogena soyoae* (deep-sea clam)	(Konishi et al., 2010a)

TABLE 21. (*Continued*)

Pterocephalus pinardii	Monoterpenoid glucoindole alkaloids and iridoids	TOF (CHCA), ESI	Structural determination. First detection of these alkaloids in Dipsacaceae	(Gülcemal et al., 2010)
Radix puerariae (Kudzu)	8-[α-D-Glc*p*-(1→6)-β-D-Glc*p*]	TOF	Identification from cultivated kudzu root	(Nguyen et al., 2009b)
Red wine	Procyanidins and anthocyanins	TOF (indole-3-acrylic acid)	Phenolic extracts shown to induce nitric oxide (NO)-mediated vasoprotectivity	(Auger et al., 2010)
Salmo salar (Salmon)	Heparin	TOF (DHB, THAP)	Structural determination and *in vivo* studies	(Flengsrud et al., 2010)
Solanum melongena (eggplant)	Xyloglycans	TOF	Further structural studies	(Kato et al., 2010c)
Streptomyces sp. strainJJ45	Disaccharide	TOF	Structural determination and antibacterial activity against *Xanthomonas* sp.	(Kang et al., 2009b)
Various commercial	Tannins	TOF (DHB)	Structural determination	(Pizzi et al., 2009)
Glycosides				
Agrostemma gracilis	Triterpene glycoside Agrostemmosides A-D.	TOF	First phytochemical report on *A. gracilis*	(Koz et al., 2010)
Albizia chinensis (Osb.) Merr.	Triterpene glycoside	TOF, ESI, GLC, ORD, IR, NMR	Structural determination. Cytotoxic to various cancer cell lines	(Liu et al., 2009f)
Albizia chinensis	Triterpene glycoside	TOF, FT-MS, GLC, HPLC, NMR	Identification of two new cytotoxic glycosides	(Liu et al., 2010e)
Albizia julibrissin	Triterpene glycoside	TOF, FAB, NMR, HPLC	Cytotoxic triterpenoid saponins acetylated with monoterpenoid acid	(Zou et al., 2010)
Anchusa azurea var. *azurea*	Triterpene glycosides (oleanazurosides and ursolazurosides)	TOF, NMR	Structural identification of four compounds	(Kuruüzüm-Uz et al., 2010)
Aralia elata	Triterpene glycoside	TOF (DHB), ESI-MS^n, NMR, HPLC	Isolation and MS fragmentation (anti-inflammatory compound)	(Lee et al., 2009h)
Astragalus amblolepis (roots)	Cycloartane-type glycosides	TOF (CHCA, LC-MS, NMR	First structural determination of GlcA moiety in cycloartanes	(Polat et al., 2009)
Astragalus icmadophilus	Triterpene glycosides	TOF (CHCA), ESI, GLC, NMR	Structural identification of six cycloartane-type glycosides	(Horo et al., 2010)
Astragalus wiedemannianus Fischer	Triterpenoid saponins	TOF	3 Cycloartane-type triterpene glycosides plus 8 known secondary metabs.	(Polat et al., 2010)
Borrelia species	Acylated cholesteryl galactosides	TOF	Found in clinically-important species, causing Lyme disease	(Stübs et al., 2009)
Bursera simaruba Sarg.	Phenolic compounds	TOF (CHCA), LC-MS	Identification and quantitative analysis	(Maldini et al., 2009)
Camellia japonica	Ellagic acid glucuronide - Okicamelliaside	TOF, IR, NMR	Isolation of potent anti-degranulation compound from leaves	(Onodera et al., 2010)
Cyclamen adzharicum (tubers)	Triterpene glycosides	TOF	Structural determination. Used in folk medicine	(Tabidze et al., 2009)

(*Continued*)

TABLE 21. (*Continued*)

Digitalis lanata	Phenylethyl glycosides	TOF	Structural determination	(Kirmizibekmez et al., 2009)
Dioscorea bulbifera	Diterpene glycosides	FT-MS, NMR	Structural determination. Three compounds (diosbulbins)	(Liu et al., 2010b)
Discodermia dissoluta	Dioctadecanoyl discoside	TOF	The first synthesis of inositol-containing marine glycolipid	(Florence et al., 2009)
Elaeodendron alluaudianum	Cardenolide glycosides	TOF, NMR	From Madagascar rainforest. Antiproliferative	(Hou et al., 2009)
Euscaphis japonica (THUNB.) KANITZ	Ellagitannin dimer	TOF (DHB), FAB	First example of isolation of ellagitannins from Staphyleaceaeous plants	(Maeda et al., 2009)
Evasterias retifera Verrill Djakonov 1938 and *E. echinosoma*	Steroid glycosides	TOF (CHCA), FAB	Structural determination.	(Levina et al., 2009)
Ferula gumosa	Sesquiterpene coumarins	TOF (CHCA) IR, UV, NMR, HPLC	Identification of two new glycosides and ten known compounds	(Iranshahi et al., 2010)
Galla Chinensis (Chinese gall)	Gallotannins	QIT-TOF (THAP/TFA)	Structural determination	(Zhu et al., 2009a)
Gleditsia aquatica	Acylated triterpenoidal saponins	TOF, ESI, FAB (sector), NMR	Structural determination. Toxic against tumors	(Ragab et al., 2010)
Glycine max (soybean)	Soyasaponins I and βg (also known as VI)	R-TOF/TOF (DHB)	As standards for quant. HPLC-MS method for soya saponins in Italian lentil seeds	(Sagratini et al., 2009)
Gypsophila paniculata L.	Triterpenoid saponins	MALDI	Identification of seven new compounds	(Yao et al., 2010)
Hippasteria kurilensis (Far East starfish)	Steroid glycosides	TOF (CHCA), ESI	Structural determination.	(Kicha et al., 2009b)
Hippasteria kurilensis	Steroid mono-glycosides	TOF (CHCA), ORD, NMR	Structural determination.	(Kicha et al., 2009a)
Holothuria forskali (sea cucumber)	Triterpene glycosides	Q-TOF (CHCA), ESI	Structural determination and distribution	(Van Dyck et al., 2009)
Holothuria forskali (sea cucumber), Cuvierian tubules	Triterpene glycosides	R-TOF/TOF, imaging	Structural determination and distribution. Specific use of MALDI-imaging	(Van Dyck et al., 2010b)
Kandelia candel and *Rhizophora mangle* (Mangrove species)	Glycosylated procyanidins from tannins	R-TOF (DHB + Cs)	Structural determination	(Zhang et al., 2010h)
Ligustrum lucidum	Secoiridoid glucosides	TOF	Compounds induce phosphorylation in cultures of cortical neurons	(Fu et al., 2010)
Linum grandiflorum (leaves and seeds)	Cyanogenic glycosides	MALDI	Structural determination. Seed oil used as medicine	(Mohammed et al., 2009)
Linum usitatissimum (flax, seed hulls)	Lignal macromolecules	TOF/TOF (DHB)	Chain length determined by incorporation of coumaric and ferulic acid glucosides	(Struijs et al., 2009)
Ornithogalum saundersiae (Liliaceae) (bulbs)	Steroid glycosides	QIT-TOF (DHB, CHCA)	Structural determination and fragmentation. Antitumor	(Kasai et al., 2009)
Panax ginseng C.A. Meyer	Ginsenosides	TOF (MnO_2 nanoparticles)	Structural determination, low background	(Sahashi, et al., 2010)
Paris delavayi	Steroidal saponins	FT-MS, NMR	Structural determination. Used in Chinese medicine as analgesic	(Zhang et al., 2009g)

TABLE 21. (*Continued*)

Pergularia tomentosa	Cardenolides	TOF (CHCA), ESI	Structural identification. Cytotoxic by inhibition of Na^+/K^+-ATPase	(Piacente et al., 2009)
Polygonatum odoratum (rhizomes)	Steroidal saponins	MALDI (CHCA), ESI	Structural determination. Used in Chinese medicine	(Wang et al., 2009c)
Populus alba Lx *Populus glandulosa* Uyeki (Suwon poplar)	Phenolic glucoside *cis*-2-OH-cyclohexyl 6-*O*-*p*-coumaroyl-β-D-Glc*p*	TOF	Structural determination	(Kim & Bae, 2009)
Populus davidiana wood	Phenolic glycoside (2-OH-cyclohexyl-6'-*O*-*p*-coumaroyl-β-D-Glc*p*	TOF, FAB, NMR	Structural determination. From tree used in folk medicine	(Si et al., 2009b)
Populus ussuriensis	Phenolic glucosides	MALDI	Structure determination. Antioxidant properties	(Si et al., 2009a)
Rubus loganbaccus x *baileyanus* Britt. (boysenberry)	Ellagitannins	TOF (DHB), NMR	Structural determination. LC-MS/MS not able to analyse compds. > 2000 Da	(Kool et al., 2010)
Ruscus colchicus (leaves)	Steroid glycosides	TOF	Structural determination. Used to treat diseases of the venous system	(Perrone et al., 2009)
Scutellaria racemosa Pers	Flavonoids	TOF, TLC, NMR	Ident. - with oligopeptidase inhibitory activity	(Marques et al., 2010)
Sea cucumbers	Saponins	Q-TOF (MALDI and ESI) (CHCA)	Analysis of saponins from five species of sea cucumber	(Van Dyck et al., 2010a)
Triumfetta cordifolia A. Rich (leaves)	Triterpenoid dimer glycoside	TOF, ESI-FT-MS-MS/MS	Structural determination. Used in Cameroon as food and traditional medicine	(Sandjo et al., 2009)
Veronica persica Poiret (flower petals)	Anthocyanins	TOF (CHCA), FAB	Structural determination and mechanism for color development in blue flowers	(Mori et al., 2009a)
Viburnum propinquum	Chalcone glycoside	TOF	Structure determination. Inhibits lipid peroxidation	(Wang et al., 2009j)
Zea mays (Mexican blue corn)	Anthocyanins	TOF (DHB, CHCA, THAP)	Identification of cyanidin-3-glucoside and pelargonidin-3-glucoside	(Castañeda-Ovando et al., 2010)
Glycolipids				
Pseudozyma tsukubaensis	Mannosyl erythritol lipid-B (MEL-B)	TOF (CHCA)	Isolation of yeast and use to produce MEL-B	(Morita et al., 2010)
Rhizochalina incrustata	Bipolar sphingolipid	TOF (DHB, CHCA)	Structural determination and biogenesis	(Makarieva et al., 2009)
Rhodococcus sp. SD-74	Succinoyl trehalose lipid (STL-1)	TOF, GC/MS, NMR	Structural determination and surface active properties	(Tokumoto et al., 2009)
Starmerella (*Candida*) *bombicola* yeasts	Sophorolipid	TOF (DHB)	MALDI-TOF method to screen for sophorolipid biosurfactants	(Kurtzman et al., 2010)
Tsukamurella pulmonis	Trehalose-containing glycolipid	FT-ICR (DHB), NMR	Structural determination and immunological study	(Paściak et al., 2010a)
Glycopeptides etc.				
Bacillus megaterium	Lipopeptides	R-TOF/TOF, TOF (CHCA)	Structural determination	(Pueyo et al., 2009)
Ipomoea batatas L. (White-skinned sweet potato)	Glycopeptide	TOF	Structural determination. 6-linked Gal oligosaccharides by MALDI as part structure	(Ozaki et al., 2010b)

(*Continued*)

TABLE 21. (*Continued*)

Other compounds				
Deep-sea yeast SY62	Mannosylerythritol lipids	TOF	For production of biosurfactants (In Japanese)	(Konishi, 2010)

[1]Format (not all items present): MALDI method (matrix), other methods.

C. Antibiotics

A novel method for the determination of aminoglycoside antibiotics used surface-assisted laser desorption/ionization mass spectrometry (SALDI MS) with the aid of silver-coated gold nanoparticles (Au@AgNPs) capped by anionic citrate. These nanoparticles were used both as concentrating agents and as matrices in SALDI MS. The LODs at signal-to-noise ratio of 3 were 3, 25, 15, 30, and 38 nM for paromomycin, kanamycin A, neomycin, gentamicin and apramycin respectively. The LODs of the first four of these antibiotics in plasma samples were 9, 130, 81, and 180 nM respectively. Recoveries of the antibiotics from plasma were about 80% (Wang et al., 2009h).

Further examples of the use of MALDI MS in the analysis of therapeutics are given in Table 24.

XIV. GLYCOSYLATION AND OTHER REACTION MECHANISMS

Applications in this section mainly involve the use of MALDI to investigate products of newly isolated enzymes. These are summarised in Table 25. Other studies are aimed at elucidating enzyme activity as illustrated by the development of a method to determine the cleavage site in small oligomannoses that has been developed by Hekmat et al. (2010). Enzymatic cleavages were performed in ^{18}O-labeled water, conditions that introduced ^{18}O into the anomeric position of the cleaved glycans. Thus, measurements by MALDI-TOF could determine if a product arose from the non-reducing end of the original oligomannose by its incorporation of the label.

The addition of a small amount of various ionic liquids has been found to modify the activity and regioselectivity of different immobilized preparations of *Rhizomucor miehei* lipase that catalyzes the hydrolysis of hexa-*O*-acetyl lactal in aqueous media (Filice, Guisan, & Palomo, 2010). The activity of the enzyme GlcNAc-transferase Vb, which transfers GlcNAc to the 6-position of the 6-antenna in *N*-glycans has been compared with that of GnT-V. One unusual product found after 8 hr was the addition of GlcNAc to the 6-position of both antennae (Alvarez-Manilla et al., 2010a).

XV. CARBOHYDRATE SYNTHESIS

Relevant reviews on carbohydrate synthesis are summarised in Table 26. Syntheses are achieved by purely chemical or enzymatic means or by a combination of both. MALDI-TOF MS is used extensively in the analysis of products; examples are listed in Tables 27 and 28. Reports of more general methods are

TABLE 22. Reviews and General Articles on the Application of MALDI to Disease

Subject	Comments	Citations	Reference
Glycomics and disease markers	Short general review	54	(An et al., 2009b)
Characterization of human genetic *N*-glycosylation defects by mass spectrometry	Much MALDI, Table of different CDGs	167	(Barone et al., 2009)
Alteration of protein glycosylation in liver disease	Mainly biochemistry of disease. Short section on MALDI	100	(Blomme, et al., 2009)
Review of methods for screening and diagnosis of CDGs	General review, *N*- and *O*-linked glycans	83	(Denecke, 2009)
Glycoproteomics in neurodegenerative diseases	Glycoprotein analysis. Large table of CSF peptides	170	(Hwang et al., 2010)
Bioanalysis of recombinant proteins and antibodies by mass spectrometry	Mainly LC/MS	89	(Ezan et al., 2009)
Determination of sialic acid and gangliosides in biological samples and dairy products	Extraction, isolation and purification. Analysis by several methods	97	(Lacomba et al., 2010)
Immunoaffinity enrichment of glycoproteins combined with MALDI-TOF for diagnostics	For detection of biomarkers and therapeutic efficiency	58	(Sparbier et al., 2009)
Proteomic and glycomic approaches to finding cancer biomarkers	General review, mainly N-glycans	55	(Taylor et al., 2009)

TABLE 23. Use of MALDI MS for Examination of Carbohydrate-Containing Compounds in Disease[1]

Disease	Medium	Methods[2]	Notes	Reference
Cancer				
Breast cancer	E-cadherin. Model in canine mammary gland adenoma	Trypsin, PNGase F, Endo H, TOF/TOF, peptides and glycopeptides	Cancer associated with highly branched *N*-glycans and increased sialylation	(Pinho et al., 2009)
Breast cancer	Breast epithelial cell line	Trypsin PNGase F, TOF/TOF (DHB), glycans (per-Me)	Principal component analysis, shows glycobiological differences between normal and cancer. Hybrid, complex glycans	(Goetz et al., 2009b)
Breast cancer	CD98hc clycoprotein	PNGase F, TOF/TOF (DHB), complex glycans (per-Me)	Identification of the glycoprotein that binds to GalMBP (fragment of mannose-binding protein)	(Powlesland et al., 2009)
Breast cancer	Serum	Trypsin, TOF/TOF (DHB), glycopeptides	Expression of *Helix pomatia* lectin binding glycoproteins in women with breast cancer in relationship to their blood group	(Welinder et al., 2009)
Breast cancer	Cells	β-Elimination (NH_4 carbamate), R-TOF/TOF (DHB), glycans, MS/MS	Use of new release method using glycoblotting and ammonium carbamate for β-elimination, Core 2 *O*-glycans	(Miura, et al., 2010b)
Breast cancer	Serum	PNGase F, reduction, TOF, R-TOF/TOF), glycans (per-Me), LC/MS	Description of chip-based LC/MS method. Increased levels of fucosylation and sialyl Lewis^x in cancer	(Alley, et al., 2010)
Breast cancer	MCF-7 Cells	PNGase F, Q-TOF (DHB, ATT, glycans, (phenylhydrazones)	Changes in glycosylation after treatment with Herceptin and Herceptin/Lipoplex. Less high mannose, more core-fucosylated biantennary glycans in cancer	(Lattová et al., 2010)
Breast cancer	MCF-7 Cells	Trypsin, Q-TOF (DHB), glycopeptides	Combined effect of treatment with antibody, cationic lipid and hyaluronic acid; *ex vivo* assays	(Bartusik et al., 2010a)
Chemically-induced tumors	Membrane stress proteins of mice	PNGase F (in-gel), TOF (CHCA), glycans (2-AB)	Differences in the sialylation patterns detected in BALB/c and IL-1α deficient mice	(Avidan et al., 2009)
Chronic myeloid leukaemia	Myeloperoxidase	Q-TOF (DHB), Glycopeptides. Glycans by Orbitrap MS/MS	Structural determination. No major differences in *N*-glycans from controls	(Ravnsborg, et al., 2010a)
Colitis-associated colon cancer	Mice	Pectinase, TOF	Apple oligogalactan ($GalA_5$) highly effective against intestinal toxicities and carcinogenesis	(Liu et al., 2010c)
Colorectal carcinoma	CD26 (dipeptidyl peptidase IV)	PNGase F (in gel), L-, R-TOF (DHB), glycans (per-Me), LC-ESI-MS/MS	All 7 sites (Asn85, 92, 150, 229, 281, 520, and 68) glycosylated. High-Man, hybrid and highly-fucosylated complex glycans	(Kawasaki et al., 2009)
Esophageal adenocarcinoma	Serum	PNGase F, TOF/TOF (DHB), glycans (per-Me)	Set of glycans identified that can be used as biomarkers.	(Mechref et al., 2009b)
Esophageal adenocarcinoma	Serum	PNGase F, TOF/TOF (DHB), glycans (per-Me)	Set of glycans identified that can be used as biomarkers	(Hammoud et al., 2010)

(*Continued*)

TABLE 23. (*Continued*)

Hepatocellular carcinoma	Serum	PNGase F, TOF/TOF (DHB), glycans (per-Me)	Changes in 57 glycans . Three *N*-glycans sufficient for detection with 90% accuracy	(Goldman et al., 2009)
Hepatocellular carcinoma	Serum glycoproteins	TOF/TOF (DHB), glycans (per-Me)	Analysis using hierarchical clustering analysis. 7 potential glycan markers identified. $Man_5GlcNAc_2$, bi-, tri-antennary	(Tang et al., 2010c)
Hepatocellular carcinoma	Serum and liver glycoproteins of rats	PNGase F, R-TOF (DHB), glycans (per-Me)	Increase in core-α-1,6-fucosylated glycoproteins. Possible biomarker	(Fang et al., 2010)
Hepatocellular carcinoma	Serum glycoproteins	TOF, CE	Core α1-6-fucosylation decreased, triantennary glycans increased	(Liu et al., 2010g)
Leukemia	Various cell lines	β-Elimination (LiOH), TOF, QIT-TOF (DHB) glycans (2-AA) -ve ion	Leukemia cells showed simple glycan profiles (sialyl-T, disialyl-T antigens). Epithelial cancer cells showed complex profiles. Core 1, 2, 3, *O*-linked	(Yamada, et al., 2009)
Lung cancer	Serum	Trypsin, SELDI (CHCA, sinapinic, G3CA, THAP/NH_4 cit), QIT-TOF (DHB), Whole glycoproteins, glycopeptides	Use of lectin-coated proteinchip arrays. High frequency of apoC-III with loss of α2→6-linked Neu5Ac in cancer patients	(Ueda et al., 2009a)
Lung adenocarcinoma	Serum	Trypsin, Q-TOF (CHCA), glycopeptides	Biomarker discovery from WGA-lectin extracted glycoproteins	(Hongsachart et al., 2009)
T-Lymphoblastoid cells	CEM cells	TOF (DHB, ATT/phenylhydrazine-HCl), glycopeptides	To study effect of monoclonal antibody treatment. Cell growth decreased after treatment	(Bartusik et al., 2010b)
Multiple myeloma	Serum	PNGase F, QIT-TOF (CHCA), glycopeptides, HPLC, glycans (2-AP)	Characterization of abnormal *N*-glycosylation on kappa chain of cryocrystalglobulin (biantennary complex)	(Toda et al., 2009)
Ovarian cancer	Tissue samples	TOF (MBCT), tissue imaging	Sulfatides found to be elevated in cancer	(Liu et al., 2010j)
Ovarian (epithelial) cancer	Plasma	β-Elimination, FT-ICR (DHB)	Development of nano-LC LTQ Orbitrap method and comparison with MALDI-FT-ICR. High-mannose, complex glycans	(Bereman, et al., 2009a)
Pancreatic cancer	Human pancreatic juice	β-elimination, TOF (DHB, glycans (per-Me)	Development of supported molecular matrix electrophoresis for glycoprotein ident. Three types of mucin detected in pancreatic juice. Mucin glycans	(Matsuno et al., 2009)
Pancreatic cancer	Serum	Trypsin, QIT-TOF (DHB), glycopeptides	Glycoproteins captured by antibody microarray. Up-regulated glycoproteins detected.	(Li et al., 2009c)
Pancreatic cancer	Serum glycoproteins	PNGase F, TOF (DHB), ESI (-ve), HPLC	Increased levels of sialyl $Lewis^X$ and branching detected on several glycoproteins	(Sarrats et al., 2010)
Pancreatic and colon cancer	Gb3Cer/CD77	IR-MALDI-o-TOF (glycerol)	Increased expression in cancer. Suggests shiga toxin as potential therapeutic agent	(Distler et al., 2009)

TABLE 23. (*Continued*)

Prostate cancer	Prostate-specific antigen and prostatic acid phosphatise, (seminal fluid)	Trypsin, chymotrypsin, PNGase F, TOF/TOF (DHB), Glycans (per-Me), glycopeptides ESI-QTrap	Structural determination. Asn-62 (complex), 188 (complex), 301 (high-mannose)	(White et al., 2009)
Prostate cancer	Glycoproteins from PC3 and LNCaP cells	β-Elimination after trypsin and PNGase F, TOF/TOF, glycans (per-Me)	Addition of core 3-glycans suppressed tumor formation and tumor metastasis	(Lee et al., 2009k)
Prostate cancer	Expressed prostatic secretions	Trypsin (beads), PNGase F, TOF/TOF (DHB), glycans (per-Me)	Detection of biomarkers by non-invasive method. (High-mannose, bi-, tri-, tetra-antennary complex)	(Drake et al., 2009)
Prostate cancer and benign prostate disease	β-Haptoglobin from prostate	PNGase F , TOF/TOF (DHB), glycans (per-Me)	Enhanced expression of mono-sialylated triantennary glycans in cancer	(Yoon et al., 2010b)
Stomach cancer	MKN45 cells, serum	Automated β-elim. (Matsuno et al., 2007), TOF (DHB), glycans (phenylhydrazones)	MKN45 cells found to express characteristic trisialo-polylactosamine-type glycans.	(Yamada et al., 2010a)
T-Lymphoblastoid CEM cells	Cells	PNGase F, Q-TOF (DHB, ATT, glycans, (phenylhydrazones)	Changes in glycosylation after treatment with Herceptin and Herceptin/Lipoplex. Less high mannose, more core-fucosylated biantennary glycans	(Lattová, et al., 2010)
Various cancers	Tumor tissue	Non-reductive β-elimination, TOF, glycans, exoglycosidase	Identification of a novel group of tumor-associated GalNAc antigens	(Satomaa et al., 2009a)
		CDG		
Alpha-dystro-glycanopathy (CDG-1)	Serum glycoproteins	PNGase F, LTQ, glycans (per-Me), ESI	Deficiency found in Dol-P-Man synthase subunit DPM3	(Lefeber et al., 2009)
Atypical hereditary fructose intolerance	Serum transferrin	TOF, glycans	Under-occupation of glycosylation sites and glycan abnormalities, reversed by fucose-free diet	(Quintana et al., 2009)
COG4-deficient (CDG-II)	Serum glycoproteins	TOF, glycans (per-Me)	Full complex glycans but decrease in sialylation	(Reynders et al., 2009)
CDG-II	Serum glycoproteins	Hydrazine, TOF (DHB), ESI-MS/MS (-ve ion)	*N*-glycans lacking a 6-antenna. Mainly study of -ve ion fragmentation	(Harvey et al., 2010)
CDG-IIL	Serum transferrin	PNGase F, TOF, Glycans (2-AB)	Deffciency of subunit 6 in COG6 complex. Lack of galactose and Neu5Ac	(Lübbehusen et al., 2010)
COG subunit 1 mutation	Serum transferrin	PNGase F, TOF, glycans (per-Me)	Cerebrocostomandibular-like syndrome. Increase in partial sialylation on biantennary glycans	(Zeevaert et al., 2009a)
COG7 Mutation	Serum transferrin	TOF, glycans	Deficiency in sialylation and smaller deficiency in galactosylation	(Zeevaert et al., 2009b)
		Other		
Anti-phospholipid syndrome	β-2-glyco-protein I from serum	Chymotrypsin, PNGase F, Q-TOF (DHB), glycopeptides	Reduced triantennary complex and increased biantennary glycans at Asn-143 in patients	(Kondo, et al., 2009)

(*Continued*)

TABLE 23. (*Continued*)

Hepatic cirrhosis	IgA from serum	Trypsin, PNGase F, TOF (DHB), glycans (per-Me), GC/MS	Increased bisecting biantennary glycans and increased core fucosylation in patients	(Carré et al., 2009)
Leishmaniasis	Sialic acid from *Leishmania donovani* promastigotes	Mild acid hydrolysis, TOF (DHB), 9-*O*-Ac-sialic acid (DMB derivs)	9-*O*-acetylated sialic acids enhance entry of virulent *Leishmania donovani* promastigotes into macrophages	(Ghoshal et al., 2009)
Liver fibrosis-cirrhosis	*N*-glycans from serum glycoproteins	PNGase F, TOF, Glycans (per-Me)	Review of *N*-glycome modifications. Importance of IgG and IgA	(Klein et al., 2010a)
Liver cirrhosis	*N*-Glycans from IgG, transferrin, antitrypsin and haptoglobin	PNGase F, TOF, Glycans (per-Me), GC/MS	IgGs are major glycoproteins involved in the modifications of total serum *N*-glycome	(Klein et al., 2010b)
Lyme disease	Lipids from *Borrelia burgdorferi* membranes	R-TOF (DHB)	Late stage patients had strong IgG response to glycolipids cholesteryl galactoside and monogalactosyl diacylglycerol	(Jones et al., 2009)
α-Mannosidosis	Lysosomal proteins in mouse model	PNGase F, TOF (DHB), Glycans	High-Man. Impaired lysosomal trimming of *N*-linked glycans leads to hyperglycosylation	(Damme et al., 2010)
Myocarditis	Serum glycoproteins	Trypsin, PNGase F, TOF (DHB, THAP), PSD, LC-MS	Mainly same high-mannose, hybrid and complex glycans between healthy and disease. Increase in branching and Fuc.	(Carpentieri et al., 2010)
Obesity	Apolipoprotein C3 from plasma	TOF (sinapinic)	Biomarker following surgery and other therapy	(Harvey et al., 2009e)
Prader-Willi syndrome	Serum transferrin (*N*-linked), apoC-III (*O*-linked)	TOF, Q-TOF (sinapinic)	No change in *N*-linked glycans. *O*-linked glycans had increased sialylation	(Munce et al., 2010)
Rheumatoid arthritis (RA)	IgG1 and IgG2, from serum	Trypsin, L-, R-TOF (CHCA) glycopeptides	Levels of galactosylation and sialylation increase in pregnancy - link with improvement in RA	(van de Geijn et al., 2009)
Rheumatoid arthritis	IgA1 O-glycans	L-TOF (DHB), glycopeptides	Decrease in GalNAc observed from arthritis patients. *O*-linked glycans	(Wada et al., 2010a)
Tuberculosis	Malto-oligosaccharides	TOF (DHB)	Self-poisoning of *Mycobacterium tuberculosis* by targeting GlgE gene in an α-glucan pathway	(Kalscheuer et al., 2010)

[1]Human unless otherwise stated.
[2]Format (not all items present): Glycan release method and/or protease, MALDI method (matrix), compounds run (derivative), other methods.

listed in Table 29 and general reactions in Table 30. Methods to change the glycosylation of a glycoprotein are common for recombinant antibiotic production as outlined above. A general method for producing homogeneous glycoproteins with eukaryotic *N*-glycosylation has been reported and involves the transfer of the *Campylobacter jejuni* glycosylation machinery to *E. coli* and production of glycosylated proteins with the key GlcNAc-Asn linkage. The bacterial glycans were then trimmed and remodeled *in vitro* by enzymatic transglycosylation to give a eukaryotic-type *N*-glycosylation (Schwarz et al., 2010).

A method for immobilization of unstable membrane-bound enzymes to a commercially available sepharose support for glycan synthesis has been published Ito et al. (2010c). It involves modification of the protein C-terminus and a transpeptidase reaction by *Staphylococcus aureus* sortase A (SrtA) has been developed. Recombinant human β1,4-galactosyltranseferase or recombinant *H. pylori* α1,3-fucosyltransferases were bound with simple aliphatic amino groups displayed on the surface of the solid support and were shown to have the required glycosyltransferase activity.

As with previous reviews in this series, two types of compound appear to be particularly suited to MALDI-TOF analysis; namely glycodendrimers and carbohydrate/protein complexes.

TABLE 24. Use of MALDI Analysis to Monitor *N*- and *O*-Glycosylation in Biopharmaceuticals and Related Materials

Biopharmaceutical and Expression System	Methods[1]	Notes	Reference
"Abatacept" (cytotoxic T-lymphocyte antigen 4) in CHO cells	PNGase F, R-TOF/TOF (s-DHB)	In contrast to previous assumptions, CHO cells shown to be capable of adding antigenic α-Gal residues to *N*-glycans	(Bosques et al., 2010)
α1-Antitrypsin (In human AGE1hn cells)	TOF	To characterize novel human cell line	(Northoff et al., 2010)
α1-Proteinase inhibitor (In *Aspergillus niger*)	Trypsin, PNGase F, β-elimination, TOF/TOF (DHB), glycans (per-Me), GC/MS	Production, purification, and characterization, Glycans = high-mannose (large antennae)	(Chill et al., 2009)
Anti-CD20 IgG1s, anti-CD20 IgG1 rituximab mutant (S239D/S298A I332E), (Human)	PNGase F, TOF	Removal of fucosylated antibody ingredients from therapeutics shown to elicit high antibody-dependent cellular cytotoxicity in blood by two mechanisms	(Iida et al., 2009)
Anti-EGFRxanti-CD3 bispecific IgG (Human in CHO cells)	PNGase F, TOF, TOF/TOF, LC-MS/MS, glycans (2-AP)	Structural determination. Complex (biantennary)	(Kim et al., 2010d)
Arylsulfatase A (In CHO, BHK, and human fibrosarcoma cells)	Trypsin, PNGase F, TOF (DHB), glycans, exoglycosidase	Site-specific analysis. Glycan profiles varied with cell type and glycosylation site. High-Man, complex (biantennary)	(Schröder et al., 2010)
CB.Hep1p(+)KDEL and CB.Hep1p(-) KDEL plantibodies (In tobacco plants)	Trypsin, TOF (DHB), ESI, glycopeptides, glycans 2-AB, exoglycosidase	Model for comparison of release and glycan analysis methods	(Triguero, et al., 2010)
Centellosides (In *Centella asiatica* plant cell cultures)	TOF	To obtain a more efficient production system. α-Amyrin, converted into centellosides by *C. asiatica* cells	(Hernandez-Vazquez et al., 2010)
Chimeric heavy chain antibodies (In HEK293 cells)	Trypsin, PNGase F, R-TOF/TOF (DHB), glycans (per-Me)	Production of antibodies and glycan analysis (biantennary complex, G0, G1, G2)	(Zhang et al., 2009b)
Cholera toxin B subunit; membrane proximal region of gp41 (In *Nicotiana benthamiana*)	Hydrazine, TOF (DHB), glycans (2-AP)	Structure determine of HIV vaccine candidate (High-mannose, paucimannosidic)	(Matoba et al., 2009)
Chorionic gonadotropin β-subunit, and others (In *Nicotiana benthamiana*)	TOF/TOF, glycopeptides	Engineering of plants for production of GalNAc-glycosylated proteins; production of protein therapeutics with mucin type *O*-glycosylation	(Daskalova et al., 2010)
Erythropoietin (Human in *Drosophila* S2 cells)	PNGase F, TOF (DHB), glycans (2-AB)	Effect on *N*-glycan profile of suppressing GlcNAc-transferase activity. Possibly contributes to paucimannosidic glycans	(Kim et al., 2009h)
Erythropoietin (In Tobacco BY2 cells)	PNGase A, TOF/TOF (s-DHB), glycans	Amount of antigenic glycans varied with growth phase, High-mannose, paucimannosidic glycans	(Yin et al., 2009)
Glargine (insulin analogue, in *Pichia pastoris*)	V8 Protease, TOF/TOF (CHCA), intact and glycopeptides	Structural determination (Up to 7 mannose residues), site analysis (Thr-8 and 30)	(Kannan et al., 2009)
Glycoproteins (In *Nicotiania tabacum* containing GlcNAc transferase III)	Pepsin, PNGase A, R-TOF/TOF (DHB), glycans	Introduction of bisecting GlcNAc suppresses 1→3-fucosylation and xylose attachment to form paucimannosidic glycans. Bisected, little paucimannosidic	(Karg et al., 2010)

(*Continued*)

TABLE 24. (*Continued*)

Glycoproteins (From *Nicotiania tabacum* containing GlcNAc transferase III)	Pepsin, PNGase A, R-TOF/TOF (DHB), glycans	Introduction of bisecting GlcNAc suppresses 1→3-fucosylation and xylose attachment to form paucimannosidic glycans	(Karg, et al., 2010)
α-L-Iduronidase (Human in seeds of *Brassica napus* and *Nicotiana tabacum*)	TOF (sinapinic), glycoprotein. GC/MS of monosaccharides	Attached carboxy-terminal ER-retention motif, SEKDEL, reduces Xyl and Fuc in *N*-glycans but has little effect on enzyme activity	(Galpin et al., 2010)
IgA1 and IgA2 (In murine melanoma cells)	PNGase F, L-, R-TOF (DHB, THAP), glycans	Structural determination. Hybrid, bi-, tri-, tetra-antennary complex.	(Yoo et al., 2010)
IgG (In CHO-K1SV, 105 cell lines)	PNGase F, MALDI, glycans, exoglycosidase	Evaluation of cell lines for production of biopharmaceuticals, $Man_5GlcNAc_2$, Complex (biantennary)	(van Berkel et al., 2009)
IgG (In HEK 293T cells)	PNGase F, R-TOF (DHB), ESI-MS/MS (-ve), glycans	Use of glycosidase inhibitor to produce IgG with $Man_9GlcNAc_2$. Effect on xtal structure and effector functions	(Crispin et al., 2009a)
IgG (Mouse in tobacco BY2 cells)	Hydrazine, TOF (DHB), glycans (2-AP)	Use of an ER retention signal (KDEL) increased high-mannose glycans but did not eliminate paucimannosidic glycans	(Fujiyama et al., 2009)
IgG (Human 29IJ6 in silkworm larva hemolymph)	PNGase F, TOF, glycans (2-AP)	Produced 8 mg per kg of larvae with recovery of 83.1%. paucimannosidic glycans	(Park et al., 2009a)
IgG (In CHO cells)	PNGase F, TOF, glycans	Production of non-fucosylated glycans by mutation (Glycans - high-Man, bi-antennary complex)	(von Horsten et al., 2010)
IgG (In CHO cells)	PNGase F, TOF	Chromatographic method to enrich non-fucosylated glycans	(Tojo, et al., 2009)
IgG (Rituximab) (In CHO-K1 cells)	PNGase F, TOF (DHB)	Molecular engineering of exocytic vesicle traffic found to enhance productivity of CHO cells	(Peng & Fussenegger, 2009)
IgG (29IJ6), (Human in silkworm)	PNGase A, TOF, glycans $Man_{12}GlcNAc_2$, $Man_6GlcNAc_2$ (2-AP)	Improved secretion of molecular chaperone-assisted IgG. No alterations in *N*-glycans	(Dojima et al., 2010)
IgG (Avastin, Ritoxan, Remicade, Herceptin (Commercial sample)	PNGase F, Q-TOF (DHB or DHB/DMA), CID, complex glycans	Enzymatic removal of galactose. Replacement with galactose containing C=O or azide at C2. Link to fluoroprobe	(Boeggeman et al., 2009)
IgG (Trastuzumab), (Commercial sample)	TOF	Efficacy of afucosylated Trastuzumab shown to be superior *in vivo* for treatment of HER2-amplified breast cancer	(Junttila et al., 2010)
IgG (L and H chains), (Murine in *Bombix mori* (silkworm) cocoons)	Hydrazine, PNGase F, R-TOF/TOF (DHB) glycans (2-AP)	Production and structural determination. (High-mannose-, hybrid, complex. No fucose)	(Iizuka et al., 2009)
IgG1 (In CHO cells)	Papain, trypsin, TOF, glycopeptide	Detection of *O*-fucose at Ser-30 of the light chain	(Valliere-Douglass et al., 2009a)
IgG1 (In CHO cells)	PNGase F, Q-TOF (DHB), LC-MS/MS, glycans	Methods for detecting differences between a candidate biosimilar and an innovator monoclonal antibody	(Xie et al., 2010)
IgG1 (In CHO cells)	PNGase F, TOF, glycans, HPLC	Host cells engineered to produce soluble sialidase	(Naso et al., 2010)
IgG1, IgG2 (*Pichia pastoris*)	TOF, glycans	Development of purification method for monoclonal antibody	(Jiang et al., 2010c)
IgG4 (In CHO cells)	PNGase F, TOF, glycans (2-AA)	Effect of culture medium components on product yield. Glycans: G1F, G2F	(Paul et al., 2009b)

TABLE 24. (*Continued*)

IgG4 (In CHO cells) IgG1 (In GS-NS0 murine cells)	PNGase F (solution and in-gel), TOF/TOF (DHB), glycans	Development of two methods, based on standard techniques, for characterization of glycosylation	(Hansen et al., 2010)
IgG (29IJ6), (Human in silkworm)	PNGase A, TOF, glycans (2-AP)	Improved secretion of molecular chaperone-assisted IgG. No alterations in *N*-glycans	(Dojima, et al., 2010)
Interferon-γ, (Human in CHO cells)	TOF, glycans (per-Me)	Study of intracellular glycosylation activities. Effects of nucleotide sugar precursor feeding	(Wong et al., 2010b)
Interferon (rhIFN- 2b mutein, 4N-IFN (Human in CHO cells)	PNGase F, TOF, glycans	Structural characterization. Complex (tetra-antennary)	(Ceaglio et al., 2010)
KIR2DL1 (human immune cell surface receptor, in *Bombix mori* (silkworm)	Endo H PNGase F, TOF, glycans (2-AP)	To evaluate silkworm as expression system for biopharmaceuticals. Simple glycosylation. Paucimannosidic glycans	(Sasaki et al., 2009b)
Lysosome-associated membrane protein 3 (In CHO cells)	TOF/TOF, Q-TOF	Use of mutant CHO cell lines established by fluorescence-activated cell sorting	(Wilke et al., 2010)
Rituximab (In HeLa and engineered HeLa-Munc18b15 cells)	PNGase F, TOF (DHB), glycans	Vesicle-trafficking protein munc18b shown to increase the secretory capacity of mammalian cells	(Peng et al., 2010b)
Single-chain hepatocyte growth factor (In CHO cells)	TOF/TOF, Q-TOF	Use of mutant CHO cell lines established by fluorescence-activated cell sorting	(Wilke, et al., 2010)
Thyrotropin (Human in CHO cells)	TOF (sinapinic), glycoprotein. Glycans by mass difference	Stable expression of a human-like sialylated recombinant thyrotropin in cell line expressing α2,6-sialyltransferase	(Damiani et al., 2009)
Transferrin (Human in *Pichia pastoris*)	Endo H, TOF (sinapinic) glycoprotein	Structural determination. $Man_{12}GlcNAc_2$, $Man_6GlcNAc_2$	(Mizutani et al., 2010)

[1]Format (not all items present): Glycan release method and/or protease, MALDI method (matrix), compounds run (derivative), other methods.

A. Synthesis of Multivalent Carbohydrates, Dendrimers, and Glycoclusters

An extensive review of dendrimers (Astruc, 2010 #7260), with a section on glycodendrimers, illustrates the breadth of this subject. Masses of the larger compounds are frequently in the range 20–50 kDa. The largest compound, based on a polyglycerol scaffold contained an estimated 222 mannose residues but the authors had difficulty obtaining a MALDI spectrum because of the high MW. Syntheses frequently involve Huisgen-type click chemistry because high-yield reactions are essential when so many carbohydrate molecules have to be attached. Table 31 lists papers reporting syntheses of glycodendrimers and similar compounds.

B. Synthesis of Carbohydrate–Protein Conjugates

Among the largest of these compounds to have been reported during the review period has involved conjugation of LPS-derived oligosaccharides to diphtheria toxin CRM_{197} protein in an attempt to develop a vaccine against invasive meningococcal disease. Conjugates with a mass of 102 kDa were analyzed by MALDI-TOF from sinapinic acid, the most widely used matrix for compounds of this type.

Conjugates can be characterized by MALDI-TOF MS but for large molecules the resolving power of most instruments is insufficient to distinguish each product and only a broad peak is observed. Whereas the center of the peak represents the mean copy number of ligands per protein, information on the dispersity of the sample is usually neglected. Patel et al. (2010) have produced a mathematical approach for calculating dispersity. By simply measuring the width at half maximum of the broad peaks that usually arise from carbohydrate–protein complexes and from the unmodified proteins, they were able to calculate the product distribution variance. Furthermore, since the area between $\pm 2\sigma$ equates to 95% of the total, $\mu \pm 2\sigma$ represents the range within which 95% of adducts exist, this gives a direct measure of dispersity.

As one example of the type of work involved with this type of compound, the glycosylation sites of O-specific polysaccharide of *Vibrio cholerae* O1, serotype Ogawa linked to BSA *via* squaric acid chemistry have been determined by MALDI-TOF/TOF MS (from CHCA). The spectra showed the presence of hapten–BSA neoglycoconjugates with different hapten–BSA ratios (4.3, 6.6, and 13.2). Sites of glycation were determined by comparison of the masses of the peptides resulting from the digestion of the BSA glycoconjugates and BSA itself using tandem MS/MS with a high-collision energy cell. The spectra

TABLE 25. Use of MALDI to Study the Products of Enzymes Action on Carbohydrates

Enzyme and source	Instrument	Notes	Reference
Glycosyltransferases			
Alternansucrase from *Leuconostoc mesenteroides*	TOF (DHB), GC/MS	Characterization of products with gentiobiose	(Côté, 2009)
Arabino-furanosyltransferase from mycobacteria	TOF, GC/MS	Involved in synthesis of arabinan domain of major mycobacterial cell envelope (lipo)-polysaccharides	(Škovierová et al., 2009)
α-L-Fucosynthases from *Sulfolobus solfataricus*	R-TOF	Fucosidase used as transferase by use of β-glycosyl azides	(Cobucci-Ponzano et al., 2009)
α1,6-Fucosyltransferase (FUT8) from baculovirus/insect cell expression system	TOF (DHB)	Enzyme, which usually fucosylates core of *N*-glycans, shown to fucosylated chitooligosaccharides	(Ihara et al., 2010a)
Galactofuranosyltransferase GlfT2 (Recombinant in *M. tuberculosis* H37Rv)	L-, R-TOF (CHCA)	Polymer length shown to be controlled by a template-independent polymerase	(May et al., 2009)
β-D-Galactoside-α1,4-Gal-transferase and β-D-Galactoside-β1,4-Gal-transferase from pigeon	TOF (DHB)	Two novel enzymes catalyzing the formation of Galα1→4Galβ1→-Galβ1–4GlcNAc	(Suzuki & Yamamoto, 2010)
GalNAc transferase 2 (human)	TOF/TOF (DHB)	Adds GalNAc to several unnatural peptides	(Yoshimura et al., 2010)
GalNAc transferase 10 (human)	TOF (DHB)	Enzyme found to have a unique GalNAc-*O*-Ser/Thr-binding site	(Perrine et al., 2009)
GalNAc transferase 20 (human)	TOF	Found in testis and brain	(Peng et al., 2010a)
GalNAc transferase from mouse colon carcinoma cells	TOF	Study of GalNAc transferases transferring GalNAc to mucin	(Kato, et al., 2010a)
β-4-GalNAc transferaseB from *Drosophila melanogaster*	TOF/TOF	Golgi targeting requires a DHHC family-related protein as a pilot	(Johswich et al., 2009)
4-α-Glucanotransferase from *Synechocystis* sp. PCC 6803	TOF (DHB)	Characterization and application to various corn starches	(Lee et al., 2009a)
N-Glycan core α1,6-fucoside β1,4-galactosyl-transferase (GALT1) from *Caenorhabditis elegans*	TOF/TOF (CHCA)	Identification of Gal-transferase adding Gal to core Fuc.	(Titz et al., 2009)
GnT-I fuzed to maltose binding protein from *Nicotiana tabacum*	TOF/TOF	Recombinant expression and characterization	(Dohi et al., 2010)
GnT-V and GnT-Vb (recombinant human. Incubations in 293T cells)	MALDI	Enzymes transfer GlcNAc to 6-position of 6-antennae in *N*-glycans. Comparisons of enzymes	(Alvarez-Manilla, et al., 2010a)
GPI-modifying β1-3-GlcNAc transferase from *Trypanosoma brucei*	R-TOF (DHB) glycans	Enzyme characterization	(Izquierdo et al., 2009)
GT8E and GT8F glycosyltransferases from *Populus tremula* × *Populus alba*	TOF	Functional orthologs of *Arabidopsis* PARVUS	(Lee et al., 2009c)
Oligosaccharyl-transferase PglB from *Campylobacter jejuni*	TOF	Overexpression and topology	(Li et al., 2010b)
Peptidyl hydroxyproline *O*-galactosyltransferase from *Arabidopsis thaliana*	TOF (CHCA), glyco-pep.	Initial enzyme in arabinogalactan synthesis	(Oka et al., 2010b)
Polyprenylphosphomannosyl synthase from *Mycobacterium tuberculosis* H37Rv, Rv3779	TOF	Involved in the synthesis of mycobacterial mannosides	(Scherman et al., 2009)

TABLE 25. (*Continued*)

α(1→3)- and α(1→6)-Sialyl transferases from marine bacteria	TOF/TOF (DHB), GC/MS	Transfers sialic acids to β-galactosides of glycosphingolipids	(Kushi et al., 2010)
Sucrose:fructan 6-fructosyltransferase from cold-resistant Patagonian grass *Bromus pictus*	R-TOF (DHB)	Characterization of enzyme associated with fructan accumulation under low temperatures	(del Viso et al., 2009)
Xyloglucan endotransglycosylases from *Tropaeolum majus* (nasturtium seeds)	TOF (DHB)	Five forms of enzyme (glycosylated)	(Stratilová et al., 2010)
Xyloglucan xyloglucosyl transferase HvXET6 from *Hordeum vulgare* L. (Barley)	TOF/TOF	Substrate specificity and catalytic mechanism	(Hrmova et al., 2009)
Xyloglucan synthesising enzymes from *Arabidopsis thaliana* in *Nicotiana tabacum*	TOF (DHB)	Subcompartment localization of side chain xyloglucan-synthesizing enzymes within Golgi stacks	(Chevalier et al., 2010)
Glycosidases			
N-Acetyl-β-D-Glucosaminidase from *Penicillium canescens*	TOF (DHB)	Isolation and biochemical characterization,	(Burtseva et al., 2010)
Cellulase Cel45A from *Trichoderma reesei*	TOF/TOF (DHB, THAP), ESI-MS/MS	Enzyme shown to catalyze hydrolysis of glucosidic bonds adjacent to mono-substituted anhydroglucose units	(Enebro et al., 2009b)
Chitinase-A from *Cycas revolute* (cycad)	TOF (DHB)	Biochemical characterization, cDNA isolation, and posttranslational modification	(Taira et al., 2009b)
Chitinase-A and B from *Serratia marcescens* strain BJL200 expressed in *E. coli* TOP10	TOF/TOF (DHB)	Effects on inhibition efficacy of allosamidin, a general competitive inhibitor of family 18 chitinases.	(Zakariassen et al., 2010)
Chitinase and *N*-acetylhexosaminidase from *Verticillium fungicola*	TOF (DHB)	effect of pH on the production of enzymes in submerged cultures	(Ramirez-Coutiño et al., 2010)
Disaccharide-specific hydrolase from *Stilbella fmetaria*	TOF (DHB, THAP, CHCA, *nor*-harmane)	Deglycosylation system of 7-*O*-linked flavonoid β-rutinosides and transglycosylation activity	(Mazzaferro et al., 2010)
Endo-β-*N*-acetylglucosaminidase from *Flammulina velutipes*	TOF (DHB)	Purification, characterization and molecular cloning	(Hamaguchi et al., 2010)
Endochitinases ASCHI53 and ASCHI61 from *Aeromonas schubertii*	TOF (sinapinic)	Isolation and characterization	(Liu et al., 2009b)
β-1,3-Endoglucanase from *Thermobifida fusca*	TOF	Characterization of activity by site-directed mutagenesis	(McGrath et al., 2009)
Endo-1,3-β-D-glucanase from *Perna viridis* (edible mussel)	TOF	Determination of catalytic properties	(Zakharenko et al., 2009)
Endo-β-1,4-mannanase from *Cellulomonas fimi*	TOF (DHB)	Use of mutations to affect mannose binding	(Hekmat, et al., 2010)
Exocellulase Cel6B from *Thermobifida fusca*	TOF	Proposal of a novel hydrolysis mechanism involving proton-transfer	(Vuong & Wilson, 2009)
ER Glucosidase II from rat liver	TOF	Found to be a broad specificity hexosidase	(Miyagawa et al., 2010)
Family GH38 α-mannosidase from *Streptococcus pyogenes*	TOF, high-Man glycans (per-Me)	Characterization. α1→3-mannosidase	(Suits et al., 2010)
β-Galactosidases from *Arabidopsis* subfamily a1	TOF	Comparative characterization	(Gantulga et al., 2009)

(*Continued*)

TABLE 25. (*Continued*)

β-Galactosidases 4 and 5 from tomato	TOF	Enzymatic activity and substrate specifcity	(Ishimaru et al., 2009)
β-Galactosidases (BgaC protein) from *Streptococcus pneumoniae*	R-TOF (DHB, ATT)	Specific for Galβ1-3GlcNAc moiety	(Jeong et al., 2009)
α-Glucosidase from *Aspergillus niger*	R-TOF (DHB)	Monitoring hydrolysis and transglycosylation activity	(Shimba et al., 2009)
α-Glucosidase from *Aspergillus niger*	TOF (THAP)	Activity towards dextrin and starch	(Ota et al., 2009)
β-Glucuronidase from *Aspergillus niger*	TOF	Isolation and substrate specificity for transglycosylation	(Kiryu et al., 2009)
β-Glycosidase from *Sulfolobus solfataricus*	TOF, GC/MS, ESI, NMR	The enzyme hydrolyzes aryl β-gluco- and β-xylosides	(Cobucci-Ponzano et al., 2010)
β-Mananase from Guar gum *(Cyamopsis tetragonolobus)*	TOF	Preparation and product characterization (in Chinese)	(Zhao et al., 2009b)
β-Mannanase from *Cocos nucifera* Linn	TOF (sinapinic, DHB)	Isolation and application to depolymerization of β-(1,4)-linked D-mannans	(Soumya & Abraham, 2010)
Mountain cedar allergen Jun a 1 from *Juniperus ashei.* Recombinant in *Nicotiana benthamiana*	R-TOF (THAP)	Shown to have pectate lyase activity	(Liu et al., 2010l)
Two xylanases from *Pseudozyma hubeiensis* (yeast)	TOF (DHB)	Produced xylooligosaccharides (DP 3-7)	(Adsul et al., 2009)
Xyloglucan-specific endo-β-1,4-glucanase from *Geotrichum* sp. M128	TOF	Crystal structure reveals key amino acid residue for substrate specificity	(Yaoi et al., 2009)
GH12 xyloglucanase from *Aspergillus niger*	TOF (DHB)	Study of substrate recognition and hydrolysis	(Powlowski et al., 2009)
Other hydrolases			
Acp (peptidoglycan hydrolase) from *Clostridium perfringens*	TOF	Implicated in cell separation and stress-induced autolysis	(Camiade et al., 2010)
CBP21 chitinase and similar enzymes from *Serratia marcescens* (bacterium)	TOF	Acts on recalcitrant crystalline chitin	(Vaaje-Kolstad et al., 2010)
CHAP domain of Cse from *Streptococcus thermophilus*	TOF	Functions as an endopeptidase to promote cell separation	(Layec et al., 2009)
Heparin/heparan sulfate *N*-sulfamidase from *Flavobacterium heparinum* in *Escherichia coli*	MALDI	Structural and biochem. investigation of catalytic N-S bond cleavage	(Myette et al., 2009b)
Heparin/heparan sulfate 6-*O*-sulfatase from *Flavobacterium heparinum* in *Escherichia coli*	MALDI	Structure and biochemistry. Investigation of enzyme active site and substrate specificity	(Myette et al., 2009a)
Kdo hydrolase from *Francisella tularensis*, *Helicobacter pylori*, and *Legionella pneumophila*	TOF (CMB)	Identification of enzyme. MALDI analysis of lipid A and core	(Chalabaev et al., 2010)
Peptidoglycan hydrolase AtlL from *Staphylococcus lugdunensis*	TOF	Characterization	(Bourgeois et al., 2009)
Other enzymes acting on sugars			
BacA from *Mycobacterium tuberculosis*	R-TOF (DHB)	Shown to be involved in the maintenance of chronic infections	(Domenech et al., 2009)
Cholinephospho-transferase from *Mycoplasma fermentans*	TOF/TOF (DHB)	Molecular cloning and expression of enzyme involved in glycol-glycero-phospholipid biosynthesis	(Ishida et al., 2009)
Hemicellulase from *Chrysosporium lucknowense* C1	TOF	Investigation of the fungus for hemi-cellulase production	(Hinz et al., 2009)

TABLE 25. (*Continued*)

Peptidoglycan *O*-acetyltransferase from *Neisseria gonorrhoeae* FA1090	L-TOF	Identification and characterization of enzyme	(Moynihan & Clarke, 2010)
Putative chitin deacetylase (ECU11_0510) from *Encephalitozoon cuniculi* (microsporidian)	TOF (DHB)	Protein shown not to be a carbohydrate deacetylase	(Urch et al., 2009)
S-Adenosyl-L-methionine dependent methyltransferase from *Haloferax volcanii*	TOF (CHCA)	Enzyme shown to methylate *N*-linked pentasaccharide	(Magidovich et al., 2010)
*Tlm*k from *Strepto-alloteichus hindustanus*	FT-ICR	Functional characterization in tallysomycin biosynthetic pathway	(Wang et al., 2009g)
Trehalose synthase from *Thermotoga maritima* DSM3109	TOF	Molecular cloning and characterization	(Ryu et al., 2010)
UDP-arabinopyranose mutase from rice	TOF (sinapinic), glycoprotein	Arg residue shown to be reversibly glycosylated with single glycosyl residue; residue needed for activity	(Konishi et al., 2010b)

[1]Format (not all items present): MALDI method (matrix), compounds studied (derivative) other methods.

showed the presence of three conjugation sites on Lys residues 235, 437, and 455, assumed to be the most accessible. The identification of y-series product ions was found to be useful for sequencing of various peptides and the a- and b-product ions confirmed the sequence of the conjugated peptides (Jahouh et al., 2010). Other examples are listed in Table 32.

XVI. MISCELLANEOUS STUDIES

MALDI-TOF analysis, combined with IR spectroscopy has demonstrated covalent modifications of chitin with silk-like proteins in the formation of shells in the mollusc *Mytilus galloprovincialis* (Weiss et al., 2009). MALDI-TOF MS has also been used as a standard against which to evaluate and optimize a Fluorophore-assisted carbohydrate electrophoresis (FACE) method for analysis of pectic oligosaccharides (Sun et al., 2009a) (Article in Chinese). Koroleva et al. (2010) have used MALDI-TOF MS to identify all the major glucosinolates that accumulate in S-cells of *Arabidopsis* leaves and flower stalks. Cell sap was diluted in 10 μL methanol and mixed 1:1 with CHCA before being spotted onto the MALDI target plate. The analysis was performed in negative-ion mode using an Ultraflex TOF/TOF instrument. Finally, Mun, Rho, and Kim (2009) have used MALDI to confirm the molecular sizes of commercial cycloamyloses and Patsos et al. (2009) have used it to detect aryl glycans in cells treated with inhibitors of *O*-glycan processing.

XVII. CONCLUSIONS

MALDI continues to be a major technique for carbohydrate analysis although electrospray is more widely used. A major advantage of MALDI is that is gives a cleaner profile of glycan mixtures because of the absence of multiple charging. New techniques, such as ion mobility have emerged to complement both MALDI and electrospray but there is still much scope for improvement in carbohydrate analysis. Surveys during the review period have highlighted the fact that many laboratories still make mistakes when assigning structures. Much of this can be attributed to assumptions made between a simple mass

TABLE 26. Reviews and General Articles Containing Applications of MALDI to Carbohydrate Synthesis

Subject	Citations	Reference
Methods (mainly enzymatic) for production of chitooligosaccharides and their potential application in medicine	184	(Aam et al., 2010)
Dendrimers. Short section on glycodendrimers but little on MALDI	1692	(Astruc et al., 2010)
Design and creativity in synthesis of multivalent neoglycoconjugates	-	(Chabre & Roy, 2010)
Methods for stereocontrolled *O*-glycosylation	62	(Ishiwata & Ito, 2009)
Synthesis of glycopeptides	25	(Kajihara et al., 2010)
Enzymatic polymer synthesis, including glycopolymers	703	(Kobayashi & Makino, 2009)
Synthesis of functional mucin glycopeptides containing both *N*- and *O*-linked glycans	15	(Matsushita & Nishimura, 2010)

TABLE 27. Use of MALDI MS for Monitoring Products of Synthetic Reactions

Carbohydrate	Methods[1]	Synthetic methods and/or comments	Reference
Monosaccharides			
4-Amido-N^5-acetyl-4-deoxyneuraminic acid	MALDI	[3 + 2]-Cycloaddition of D-mannose-derived nitrone and methyl acrylate	(Gao et al., 2009b)
Aminated xyloglucan (from tamarind)	TOF (DHB)	Physico-chemical properties of aminated xyloglucan extracted from tamarind seed	(Simi & Abraham, 2010c)
Bridged C-furanosides	TOF	Intramolecular nucleophilic attack of BzO group in a triflated cyclooctenol	(Jürs & Thiem, 2009)
1-Deoxynojirimycins with dansyl capped *N*-substituents	TOF	As probes for Morbus Gaucher affected cell lines	(Fröhlich et al., 2010)
2,3-Dibromo-3-methyl-1-phenylphospholane 1-oxide	TOF	As novel anticancer agent	(Yamada et al., 2010b)
(α-D-Gal)phenylmethane and α-,β-di-F-Me analogues	TOF, LC-MS	Synthesis and conformational analysis. Interactions with the plant lectin viscumin	(Kolympadi et al., 2009)
4-*O*-Glycosylated 1,5-anhydro-D-fructose and 1,5-anhydro-D-tagatose	TOF (DHB)	Synthesised from the common intermediate 2,3-*O*-isopropylidene-D-fructose	(Agoston et al., 2009)
Glycosyl azides	TOF	Synthesis, for enzymatic transglycosylations	(Křen & Bojarová, 2010)
Haloacetamidyl oligosaccharide derivatives	TOF	As potential inhibitors of cytoplasmic peptide: *N*-glycanase (PNGase)	(Miyazaki et al., 2009)
L-Iduronic acid thioglycosides	MALDI	Synthesis of six differentially protected thioglycosides from a common precursor	(Bindschädler et al., 2010)
ManNAc esterified with short-chain fatty acids	TOF	As drug candidates	(Elmouelhi et al., 2009)
Per-^{13}C-Ac labelled monosaccharides	TOF	For NMR studies	(Vermillion & Price, 2009)
Quaternary *N*-(1,4-anhydro-5-deoxy-D,L-ribitol-5-yl)ammonium salts	TOF (CHCA)	Removal of the isopropylidene-protecting group from 1,4-anhydro-2,3-*O*-isopropylidene-5-*O*-tosyl-D,L-ribitol and from quaternary ammonium salts	(Dmochowska et al., 2009)
N-(2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl)-N'-acetylthiourea	TOF	Synthesis by treatment of *N*-(tetra-*O*-acetyl-β-D-glucopyranosyl)-N'-acetylthiourea with concentrated HCl/MeOH	(Somogyi & Batta, 2009)
Oligosaccharides			
Acarbose-fructoside	TOF (DHB)	Synthesis, structural analysis and properties	(Nam et al., 2009)
N-Acetylchitooctaose biocytin hydrazide	TOF (DHB)	Synthesis by reductive amination. For characterization of receptor-binding proteins,	(Shinya et al., 2010)
N-acetyl chitooligosaccharides	TOF (DHB)	By conversion of squid pen by *Pseudomonas aeruginosa* K187 fermentation	(Wang et al., 2010b)
β-(1→6)-D-*N*-Acetylglucosamine oligosaccharides	TOF, ESI	Synthesis of polysaccharide intracellular adhesins using an acid reversion reaction of *N*-acetylglucosamine in HF-pyridine	(Leung et al., 2009)
Amino-bridged oligosaccharide mimetics	R-TOF (DHB), FAB	Synthesis using reductive amination. Glycomimetic target structures as potential ligands for the receptor protein NKR P1 of natural killer cells	(Neumann & Thiem, 2010)
Amylose chains	TOF	From starch by action of phosphorylase. Preparation of A-type crystals	(Montesanti et al., 2010)
Bi-fluorescently-labeled maltooligosaccharides	TOF	For amylase assays	(Oka et al., 2010a)
Bis-hydrazides	TOF	For conjugation with proteins etc.	(Adak et al., 2010)

TABLE 27. (*Continued*)

Blood group tetrasaccharides B (types 1, 3 and 4)	TOF	3-Aminopropyl glycosides of tetrasaccharides synthesised using acetylated Galα(1→3)-(Fucα(1→2))Gal trichloroacetimidate as a glycosyl donor	(Korchagina et al., 2009)
3,6-Branched arabinogalactan-type tetra- and hexa-saccharides	TOF	For investigation of monoclonal antibodies raised against arabinogalactan proteins from pressed juice of *Echinacea purpurea*.	(Fekete et al., 2009)
Carboxymethylated cyclosophoraose	TOF	As a novel chiral additive for the stereoisomeric separation of flavonoids by CE	(Jeon et al., 2010)
Chitooligosaccharides	TOF	By the enzymatic hydrolysis of chitosan	(Xie et al., 2009)
Chitooligosaccharides	TOF	By the enzymatic hydrolysis of chitosan	(Xu et al., 2010a)
Chitooligosaccharides	TOF/TOF (DHB) glycans (AMAC)	Characterization of family 46 chitosanase from *Streptomyces coelicolor* A3(2) and use for degradation of chitosans	(Heggset et al., 2010)
Chitooligosaccharides	TOF	To study the antibacterial activity against bifidobacteria	(Šimůnek et al., 2010)
Chitosan and chitooligosaccharides	FT-MS (DHB)	Adsorption properties for uranium (Paper in Chinese)	(Jiang et al., 2010b)
Chitosans	TOF	Synthesis from lobster chitin by NaOH deacetylation and enzymatic hydrolysis. To protect crops from main pathogens	(Falcón et al., 2010)
Chito-tetrasaccharide β-1,4-GlcNAc-β-1,4-GlcN repeat	TOF (DHB)	By condensation of two disaccharides	(Kawada & Yoneda, 2009)
Deacetylated chitohexaose	TOF	Hydrolysis of chitosan. Could limit cell proliferation of breast cancer cells	(Xiong et al., 2009)
2-Deoxy cyclic and linear oligosaccharides	TOF (DHB)	Synthesis by oligomerization of monomers	(Paul et al., 2009a)
β-D-Fructopyranosyl-(2→6)-D-glucopyranose	TOF	Synthesis from D-glucose and D-fructose by thermal treatment	(Yamamori et al., 2010)
Galactofuranose oligomers	TOF/TOF (CHCA)	To probe mechanism by which polymer length is controlled in mycobacteria	(Splain & Kiessling, 2010)
Galactomanno oligosaccharides	TOF	From hydrolysis of guar gum by β-mannosidase (Paper in Chinese)	(Zhao, et al., 2009b)
Galactooligosaccharides	FT-MS, GC/MS	Synthesis by acid hydrolysis of the polysaccharides from *Nerium indicum* Mill	(Hu et al., 2009)
α-Glucan pentasaccharide from *Aconitum carmichaeli*	TOF/TOF (DHB)	Use of chiral-auxiliary-mediated 1,2-*cis*-glycosylations for the solid-supported synthesis	(Boltje et al., 2010)
Glucan with α -(1→6) linkages and α -(1→3) and α -(1→4) branch points	Q-TOF	Produced from glucan of *Leuconostoc mesenteroides* NRRL B-742 by microwave assisted hydrolysis	(Majumder et al., 2009)
Glucosylated raffinose	TOF (DHB)	Use of glucansucrase (alternansucrase) for synthesis	(Côté et al., 2009)
Glc-Glc, Gal-Gal, Gal-Glc, Gal-Gal disaccharides	TOF (DHB)	16-member library containing all regioisomers. Solid-phase synthesis	(Ágoston et al., 2009b)
Linear isomalto-oligosaccharides (DP2-10)	TOF	One-step synthesis using synthetic fusion enzyme of dextransucrase and dextranase	(Kim et al., 2009e)
Macrocyclic oligosaccharides	TOF	Copper(I)-catalyzed Huisgen's 1,3-dipolar cycloaddition of alkyne and azide provides size-defined macrocyclic carbohydrates	(Muthana et al., 2009)
Mannose-capped disaccharide with a thiol terminus	TOF, ESI	To provide a tethered sugar for attaching to gold nanoparticles to mimic carbohydrate-involved cell-surface interactions	(Wang et al., 2009b)

(*Continued*)

TABLE 27. (*Continued*)

Mannosides from *N*-glycans of gp-120	TOF (DHB, THAP)	Chemical stereochemically controlled synthesis	(Pastore et al., 2010a)
Nigerose-containing oligosaccharide	TOF/TOF (CHCA)	By transglycosylation reaction of maltodextrin glucosidase (MalZ) from *Escherichia coli*	(Song et al., 2010)
Non-glycosidically linked pseudodisaccharides	TOF (THAP)	Thioethers, sulfoxides, sulfones, ethers, selenoethers, and their binding to lectins	(Cumpstey et al., 2010)
Oligosaccharides from red seaweed polysaccharides	TOF (CHCA), ESI	Efficient conversion of galactans into *C*-glycosyl aldehydes	(Ducatti et al., 2009)
Oligosaccharide mimics of sialyl Lewis A	TOF (THAP)	Trisaccharide. Neu5Ac and Fuc replaced with HSO_3 and D-Ara respectivly	(Jakab et al., 2010)
Pentasaccharide anticoagulant (Idraparinux)	MALDI	Compound is fully *O*-sulfated, *O*-Me mimic of antithrombin III binding domain of heparin	(Chen & Yu, 2009)
N-Quaternary chitosan derivatives	TOF	Synthesis, characterization and antibacterial activity	(Rúnarsson et al., 2010)
Sialylated lactosides	TOF (DHB), per-Me	For coupling to BSA by Huisgen reaction. As glycocongugate antigen	(Mosley et al., 2010)
Sialyllacto-*N*-tetraose and sialyllacto-*N*-neotetraose	TOF	Use of α2-3- and α2-6-sialylated lactosaminide precursors obtained by enzymatic procedures with glycosylations employing triflic acid/*N*-iodosuccinimide	(Schmidt & Thiem, 2010)
Sucrose-based guanidine-containing G7 molecular transporters	TOF	Show different patterns of intracellular localization depending on the nature of the linker chains as well as the fluorescent dyes	(Lee et al., 2009l)
Sulfated oligofucosides	MALDI	Synthesis of sulfated octyl tetra- to octa-oligofucosides with different sulfation patterns	(Zong et al., 2010a)
α-(2→9)-Tetrasialic acid	MALDI	Use of 5-*N*,4-*O*-carbonyl-7,8,9-tri-*O*-chloroacetyl-protected sialyl donor for stereoselective synthesis	(Lin et al., 2010a)
Triazole-linked 1,6-α-D-oligomannosides	TOF (CHCA)	Aimed at inhibitors of *Mycobacterium tuberculosis* cell wall synthetase	(Lo Conte et al., 2010)
1H-1,2,3-Triazol-1-yl thiodigalactoside derivatives	TOF (DHB)	As high affinity galectin-3 inhibitors	(Salameh et al., 2010)
Two-faced *β*-1,4-glucan	TOF (DHB)	Synthesis of chitosan derivative repeating 2-azido-3,6-di-*O*-Bz-2-deoxy-β-D-Glc*p*-(1→4)-3,6-di-*O*-Bz-2-deoxy-2-phthalimido-D-Glc*p*	(Kawada et al., 2009)
Urea-linked glucosamine dimer	TOF (DHB)	As a building block for the synthesis of linear and cyclic neosaccharides	(Cirillo et al., 2010b)
Xyloglucans (non-natural)	TOF (DHB)	By polycondensation of 4,6-dimethoxy-1,3,5-triazin-2-yl oligosaccharide monomers catalyzed by endo-*β*-1,4-glucanase	(Tanaka et al., 2010c)
Polysaccharides			
Cellulose acetate derivatives with disulfide group	R-TOF (DHB)	For preparation of self-assembled gold nanoparticles	(Enomoto-Rogers et al., 2010)
Cellulose nanocrystals grafted with poly(ethylene oxide)	R-TOF (dithranol)	To achieve steric instead of electrostatic stabilization. Two-step synthesis	(Kloser & Gray, 2010)
Cyclic β-glucan	R-TOF/TOF (CHCA)	Synthesis using laminarinase 16A glycosynthase mutant from the basidiomycete *Phanerochaete chrysosporium*	(Vasur et al., 2010)
Dextrin-hydroxyethyl-methacrylate and dextrin-vinyl acrylate hydrogels	TOF/TOF (DHB)	For the determination of biocompatibility and biodegradability in mice	(Moreira et al., 2010)

TABLE 27. (*Continued*)

Epoxy-starch derivatives	TOF (DHB)	Synthesis by epoxidation of allylated starch	(Huijbrechts et al., 2010)
Poly-*N*-acetyllactosamine	TOF (DHB, CHCA)	Chemo-enzymatic synthesis. Characterization for CGL2-galectin-mediated binding of ECM glycoproteins to biomaterial surfaces	(Sauerzapfe et al., 2009)
Triblock co-oligomers of tri-*O*-methylated and unmodified cello-oligosaccharides:	TOF (DHB)	Synthesis and structure-solubility relationships	(Kamitakahara & Nakatsubo, 2010)
Xylan-based polysaccharides	TOF (DHB)	Amino-modified low MW xylan reacted with unmodified xylan and cellodextrins	(Daus & Heinze, 2010)
Glycosaminoglycans and related compounds			
N-Acetyl-heparosan oligosaccharides	TOF	Digestion of *N*-acetyl-heparosan with heparitinase. for study of enzymology	(Sugiura et al., 2010a)
2,3-Desulfated heparin	MALDI	For control of inflammation by inhibition of E-selectin	(Lakshmi et al., 2010)
Heparan sulfate oligosaccharides	TOF/TOF (DHB), ESI	Use of modular building blocks for preparation of a library of 12 oligosaccharides Used to probe the structural features of HS for inhibiting the protease, BACE-1	(Arungundram et al., 2009)
Heparan sulfate oligosaccharides	TOF	Synthesis and inhibition of endothelial cell functions essential for angiogenesis	(Cole et al., 2010)
Hyaluronan	TOF	For NMR study of chemical proton exchange over the β(1→3) glycosidic linkage	(Nestor et al., 2010)
Hyaluronic acid decasaccharide	MALDI	Chemical synthesis using preactivation-based chemoselective glycosylation strategy	(Lu et al., 2009)
Hyaluronic acid subunit and fully protected oligomers	MALDI	Tetra-, hexa- and octa-saccharides. Multi-gram synthesis	(Virlouvet et al., 2010)
Isosteric sulfonate analogues of AT-III binding domain of heparin	TOF (THAP)	D-GlcA- and L-IdoA-containing disaccharide. related to antithrombin-binding pentasaccharide of heparin. One sulfate ester replaced by Na sulfonato-Me moiety	(Herczeg et al., 2009)
***N*-linked glycans**			
Bisected octasaccharide	MALDI	Chemical synthesis	(Wang et al., 2009e)
Galβ(1→3)[NeuAcα(2→6)] GlcNAcβ(1→2)Man motif	TOF	Chemical synthesis as molecular probe	(Bao et al., 2010)
Glucuronyl oligosaccharides	TOF, glycans (2-AP)	Synthesis of glucuronyl and sulfoglucuronyl oligosaccharides from HNK-1 glycoprotein	(Yagi et al., 2008)
High-mannose glycans	TOF (DHB)	Related to HIV gp120. One-pot catalytic glycosidation/Fmoc removal	(Pastore et al., 2010b)
High-mannose glycans with Glc_3 units	TOF (DHB)	Study of the conformational properties of the Glc_3Man unit	(Mackeen et al., 2009)
High-mannose glycans - methotrexate derivatives	TOF	Identification of the recognition motif of the glycoprotein-folding sensor enzyme, UDP-Glc: glycoprotein glucosyltransferase	(Totani et al., 2009)
N-glycan clusters	TOF (DHB)	Biantennary and high-mannose *N*-glycans linked to non-reducing terminus of $Man_3GlcNAc_2$ core, plus biotin for arrays	(Huang, et al., 2009a)
N-Glycan library	TOF (DHB), glycans (2-AP)	Enzymatic construction of library for building MS database	(Ito, et al., 2010a)
Phosphorylated high-mannose glycans	TOF	High-mannose glycans from ribonuclease. Incubation with recombinant GlcNAc phosphotransferase.	(Bohnsack et al., 2009)

(*Continued*)

TABLE 27. (*Continued*)

Phosphorylated high-mannose glycans, AEAB derivatives	R-TOF	High-mannose glycans from ribonuclease. Incubation with recombinant GlcNAc phosphotransferase. For glycan microarrays	(Song, et al., 2009f)
Sialic acid containing complex-type *N*-glycan	TOF	New solid-phase synthesis. Stereoselective β-mannosylation, microfluidic α-sialylation and glycosylation of *N*-PhF_3acetimidate on JandaJel resin	(Tanaka et al., 2009)
Thiol-terminated nonamannoside	TOF	For synthesis of microarrays	(Dietrich, et al., 2010)
Various complex glycans	TOF	Development of HEK393T expression system for human glycosyltransferases	(Chiba et al., 2010)
_O_-linked glycans			
O-*N*-Glycan library	TOF (DHB), glycans	Enzymatic construction of library for building MS database	(Ito, et al., 2010a)
Glycosylated amino acid derived from PSGL-1	TOF	Use of trichoroacetimidate donors and thioglycosyl acceptors	(Vohra et al., 2009)
KL-6 antigen	TOF/TOF (DHB)	Library of glycans to determine binding to anti-MUC1 antibody	(Ohyabu et al., 2009)
Glycopeptides/Glycoproteins			
Aglycoristocetin derivatives containing hydrophobic side chain-substituted cyclobutenedione.	TOF (DHB)	Synthesis and anti-influenza activity	(Naesens et al., 2009)
Androgenic gland hormone of the woodlouse, (*Armadillidium vulgare*)	TOF	With various glycans. Showed that thermodynamically most stable form not most active: Result of disulfide pairing	(Katayama et al., 2010b)
Antifreeze glycopeptide analogues	TOF (DHB, CHCA)	Microwave-enhanced synthesis and functional studies	(Heggemann et al., 2010)
β-hFSH with chitobiose units at the natural linkage sites	TOF	Use of the Sinaÿ radical glycosidation for simultaneous installation of biantennary chains and glycal chemistry to construct the tetrasaccharide core	(Nagorny et al., 2009)
β-Sheet-rich protein plus GlcNAc at various positions	TOF	Effect of GlcNAc position on protein folding kinetics and thermodynamics	(Price et al., 2010a)
Biantennary *N*-glycans plus peptide	TOF/TOF (DHB)	Solid-phase peptide synthesis. Glycans linked -NH-CO-CH_2-S-Peptide	(Murase et al., 2009)
Bivalent glycopeptide	TOF	Mannosides linked with squaric acid	(Lindhorst et al., 2010a)
CD52 Glycopeptide antigens	TOF (DHB, CHCA)	Chemo-enzymatic synthesis of glycopeptide with *N*- and *O*-linked glycans	(Huang et al., 2010c)
C-glycosyl β^2- and β/β^2-peptides	MALDI	Solution-phase synthesis. 3-8 amino acids	(Inaba et al., 2009)
C-Linked antifreeze glycoprotein analogues	TOF (DHB)	Effect of the length of the amide-containing side chain between the carbohydrate moiety and the polypeptide backbone influences ice recrystallization inhibition	(Tam et al., 2009)
C-Mannosylated peptides	TOF (DHB, CHCA)	Peptides shown to interact with Hsc70 to modulate its signaling in RAW264.7 cells	(Ihara et al., 2010b)
Cyclic antifreeze glycopeptides	TOF	Exhibited antifreeze activity by forming hexagonal-bipyramidal ice crystals	(Hachisu et al., 2009)
Cyclic neoglycopeptides	MALDI (CHCA)	For binding to adjacent protein binding sites in wheat germ agglutinin	(Schwefel et al., 2010)
Dihydrofolate reductase	TOF	Glycans = GlcNAc, lactose, maltotriose Analysis as tryptic peptides. For study of effects of glycosylation on stability	(Tey et al., 2010)

TABLE 27. (*Continued*)

^{18}F-Labeled galacto and PEGylated arginine–glycine–aspartic acid dimers	TOF	For positron emission tomography (PET) imaging of $\alpha_v\beta_3$ integrin expression	(Liu et al., 2010f)
Fluorescein-labelled *O*-dimannosylated peptides	TOF (CHCA)	Microwave-assisted synthesis. 5(6)-Carboxyfluorescein shown to be stable	(Kowalczyk et al., 2009)
Fmoc-threonine bearing a core-2 glycan	TOF	As building block for PSGL-1 *via* Fmoc-assisted solid-phase peptide synthesis	(Krishnamurthy et al., 2010)
O-Fucosylated epidermal growth factor-like repeat 12 of mouse notch-1 receptor	TOF (DHB)	Chemical synthesis and studies on folding	(Hiruma-Shimizu et al., 2010)
Galactosylated naringinase	TOF (sinapinic)	Modification of glycosylation to effect deglycosylation of rhamnosylated drugs	(Garnier et al., 2010)
Gal-β-3GalNAc-α-Lys_5	TOF	Immunogen design for tumor T antigen immuno-targeting	(Sendra et al., 2009)
Glycopolypeptide-based cholera toxin inhibitors	MALDI	Effect of peptide charge and glycan linker length on activity	(Maheshwari et al., 2010)
Glycopeptide carrying tetra-*N*-Ac-lactosamine containing core 2 decasaccharide	TOF (DHB)	Solid-phase synthesis	(Ueki et al., 2010)
Glycosaminoglycan-protein linkage tetraosyl peptide moieties of betaglycan	TOF	To investigate structures that best serve as a hexosamine acceptor for enzymatic glycosyl transfer	(Tamura et al., 2010)
Glycosulfopeptides from *N*-terminus of human endoglycan	TOF/TOF (THAP)	Containing tyrosine sulfate residues and sialyl Lewis x in core 2 *O*-glycans and bind to human L-selectin	(Leppänen et al., 2010)
Glycosylated peptoids	TOF	By on-resin click (Huisgen reaction) glycoconjugation	(Norgren et al., 2009)
Glycosylated cell-penetrating peptide (R6/W3): Ac-RRWWRRWRR-NH_2	TOF	One, two, or three galactose(s), with or without a spacer introduced *via* a triazole link	(Dutot et al., 2010)
GRGDY grafted to chitosan	TOF (CHCA)	Linked with sulfosuccinimidyl-6-[4'-azido-2'-nitropheny-lamino]hexanoate as drug carrier	(Yang et al., 2010i)
N-Glycosylated insulin	L-TOF (DHB)	Addition of three GlcNAc residues at NH_2 groups on peptide. Use of Endo M to transfer glycan to one of them.	(Tomabechi et al., 2010a)
N-Glycoproteins carrying intact natural *N*-glycans	TOF/TOF (DHB)	Enzymatic synthesis of biantennary glycans	(Huang et al., 2009b)
Glycosylated analogues of glucagon-like peptide 1	TOF, LC-MS	To improve proteolytic stability and blood glucose-lowering activity. Sugars = GlcNAc, LacNAc, sialyl LacNAc synth. by chemoenzymatic approaches	(Ueda et al., 2009b)
Glycosylated neurotensin analogues	TOF	Containing *O*-linked β-melibiose and α-TF antigen or β-lactose units linked by a PEG3 spacer. Exhibit subpicomolar anticonvulsant potency in model of epilepsy	(Lee et al., 2009f)
Glycosylated tetracontapeptide with acid-labile sialyl-T_N antigens	MALDI (DHB)	20-Residue glycopeptide-α-thioester and 20-residue glycopeptide with Cys at N-terminal. Solid phase synthesis; coupled by ^{Cys}NCL^{Ser}.	(Okamoto et al., 2009)
O-Glycopeptide mimetics	TOF (DHB, CHCA)	Aziridine ring opening as regio- and stereoselective access to *O*-glycosyl amino acids and their transformation into *O*-glycopeptide mimetics	(Schäfer et al., 2009)
Heptasaccharide from *Campylobacter jejuni* plus AcrA61-210	TOF/TOF (CHCA)	Development of NMR method for 3D structural determination of glycoproteins using enzymatically synthesised glycoprotein	(Slynko et al., 2009)

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TABLE 27. (*Continued*)

Hydrolytically stable bioactive glycopeptide homo- and co-polymers	TOF (DCTB)	Synthesis by combination of ring-opening polymerization of amino acid *N*-carboxyanhydrides and Huisgen click reaction	(Huang et al., 2010b)
4-OH-proline oligomers	Q-TOF (DHB)	Compounds form very stable polyproline II helices	(Owens et al., 2010)
IgA-hinge peptide	TOF	To study effect of glycosylation on *cis*/*trans* isomerization of prolines (by NMR)	(Narimatsu et al., 2010b)
$Man_{5\text{-}9}GlcNAc_2$-Asn-*N*-^{14}C	R-TOF (DHB)	For micro-method for determining precise oligosaccharidic specificity of mannose-binding lectins	(Debray et al., 2009)
Mannosylated lysine derivative	TOF	Bivalent carbohydrate branching unit. Suitable for solid-phase peptide synthesis	(Schierholt & Lindhorst, 2009)
Mouse pro-opiomelanocortin(1–74)	TOF	Synthesis by azido-protected glycopeptide ligation *via* the thioester method	(Katayama et al., 2010a)
MUC1 glycopeptide with GPI anchor	TOF	MUC1 glycopeptide coupled to GPI derivatives by sortase A verifying that SrtA can accept sterically hindered glycopeptide as substrate	(Wu et al., 2010d)
Murine podoplanin *O*-glycopeptide	TOF, ESI (Orbitrap)	Found to be highly immunogenic in mice. Cancer specific	(Steentoft et al., 2010)
Mucin-like glycopeptide antigen analogues	TOF (DHB)	Fluorinated amino acids incorporated into MUC1 glycopeptide	(Wagner et al., 2010)
Neoglycopeptides, MUC1 glycoprotein with core 2 *O*-glycan + complex *N*-glycan	TOF (DHB)	Synthesis by integrating chemical and enzymatic approaches on functional polymer platform	(Matsushita et al., 2009)
Oxazole-modified glycopeptides	TOF	For targeting arthritis-associated class II MHC A^q and DR4 proteins	(Andersson et al., 2010)
Peptides labelled with 2-[^{18}F]fluoro-2-deoxy-D-Glc	TOF	For introduction of ^{18}F label	(Wuest et al., 2009)
Poly-acridine peptide plus $Man_9GlcNAc_2$	TOF (DHB)	MALDI to check $Man_9GlcNAc_2$ released from soybean agglutinin	(Anderson et al., 2010)
Sialic acid-derived α/δ-peptides	TOF	Half-life in blood is two- to three-orders of magnitude higher than natural α-peptides	(Saludes et al., 2010)
Sialylated ribonuclease C	TOF	By transglycosylation with complex-type *N*-glycan oxazolines catalysed by *Arthrobacter* endo-β-*N*-acetylglucosaminidase	(Huang et al., 2010d)
Sialylated glycoproteins	TOF	Transglycosylation with *Mucor hiemalis* endoglycosidase and synthetic sialo-complex-type sugar oxazoline	(Umekawa et al., 2010)
Sialoglycopeptide	L-TOF (sDHB)	For blocking influenza virus infection. Use of rat α2,6-sialyltransferase	(Ogata et al., 2009)
Skp1	TOF (sinapinic)	Chemical synthesis, for enzymatic study in *Dictyostelium* (see Table 12,*O*-glycans)	(Wang, et al., 2009k)
S-Linked glycopeptides	MALDI	Thioglycosylated building blocks prepared from per-Ac sugars *via* glycosyl iodides in one-pot fashion and used in sub-monomer solid phase strategy	(Comegna & De Riccardis, 2009)
Thiourea-tethered *C*-glycosyl amino acids	TOF (CHCA), ESI	Synthesis *via* isothiocyanate-amine coupling	(Barghash et al., 2009)
Tn3-glycopeptides	TOF (CHCA, DHB)	For isolation and characterization of antibodies from a phage library	(Sakai et al., 2010)
Tn antigen (pentavalent GalNAc-containing glycopeptide)	TOF	Solid-phase synthesis. Representing the nephropathy-associated IgA hinge region	(Bolscher et al., 2010)

TABLE 27. (*Continued*)

Urea-tethered glycosylated amino acids, glycopeptides	TOF	Reaction mediated by di-Ph phosphoryl azide using N^{α}-Fmoc-Asp/Glu-5-oxazolidinones	(Nagendra et al., 2009)
Carbohydrates from bacteria			
Bacillus anthracis tetrasaccharide with thiol linker	MALDI	For attachment to a maleimide functionalized Microarray to study of carbohydrate-antibody interactions by array	(Oberli, et al., 2010)
α-Cyclosophorohexadecaose (α-C16)	TOF	Extracted from *Xanthomonas oryzae*. For preparation of multi-wall carbon nanotube-coated glassy carbon electrode	(Jin et al., 2010)
6-Deoxytalose-containing tri- and hexasaccharides from O-antigen of *Mesorhizobium huakuii* IFO15243T	MALDI	Chemical synthesis from L-rhamnose. As *p*-methoxyphenyl glycosides.	(Zong et al., 2010c)
Di- and tetrasaccharide from the O-chain of *Burkholderia pseudomallei* strain 304b	TOF	Disaccharide = β-D-Glc*p*-(1→3)-6-deoxy-α-L-Tal*p*	(Yan et al., 2009)
GlcNAc-pyrophosphate-lipid analogs of GlcNAc-pyrophosphate-undecaprenol acceptors	TOF	For studies of the acceptor specificities of O-antigen biosynthetic enzymes	(Riley et al., 2010)
6-Deoxytalose tetrasaccharide from O-glycan of *Aggregatibacter actinomycetemcomitans*	MALDI, ESI	As *p*-methoxyphenyl glycoside for glycogonjugate formation.	(Cai et al., 2010)
Heptasaccharide repeating unit from *Klebsiella oxytoca* BAS-10	TOF	Synthesis of the iron-binding exopolysaccharide using a block synthetic strategy	(Guchhait & Misra, 2009)
Kdo_2–Lipid A $^{13}C,^{15}N$-labelled from *Escherichia coli*	TOF	NMR spectral mapping of Lipid A molecular patterns affected by interaction with the innate immune receptor CD14	(Albright et al., 2009)
Lipoteichoic acid core from *Streptococcus pneumoniae*	TOF (DHB (+), THAP (-))	Synthesis of Glcβ-(1-3)-2-acetamino-4-amino-2,4,6-trideoxy-Gal-β(1-3)Glcα(1-*O*)-diacylglycerol	(Pedersen et al., 2010)
LPS hexasaccharide from *Azospirillum irakense* KBC1	MALDI	Chemical synthesis by 4 + 2 block glycosylation strategy	(Ghosh & Misra, 2010)
Monophosphoryl lipid A adjuvant candidates	TOF	Chemical synthesis and proinflammatory responses	(Maiti et al., 2010)
Monophosphoryl lipid A from *Escherichia coli* coupled to *N*-modified GM3	TOF, ESI	Synthesis of monophosphoryl lipid A and coupling by click chemistry.	(Tang et al., 2010b)
O86 Oligosaccharide repeating unit	TOF, glycans (2-AB)	Defining enzyme functions in *in vitro* polysaccharide biosynthesis	(Woodward et al., 2010)
Pentasaccharide part of Skp1 glycoprotein from *Dictyostelium discoideum*	R-TOF (THAP), ESI	2+3 Block syntheses using the disaccharide donor at the non-reducing end, and three different trisaccharide acceptors at the reducing end	(Szabó et al., 2009)
Pentasaccharide repeating unit of *Escherichia coli* O128 antigen	TOF (CHCA	Synthesis *via* a convergent '2+3' glycosylation strategy	(Lv et al., 2010)
Penta- and hexa-saccharides from the O-antigen of *Escherichia coli* O150	MALDI, ESI	Convergent chemical synthesis. [3+2] block method. For later synthesis of glycoconjugates	(Panchadhayee & Misra, 2010a)
Penta- and hexa-saccharides from the O-antigen of *Escherichia coli* O150	MALDI	Sequential glycosylation with [3+3] block method	(Panchadhayee & Misra, 2010b)

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TABLE 27. (*Continued*)

Pentasaccharide part of Skp1 glycoprotein from *Dictyostelium discoideum*	R-TOF (THAP), ESI	2+3 Block syntheses using the disaccharide donor at non-reducing end, and three different trisaccharide acceptors at the reducing end	(Szabó, et al., 2009)
Polyprenyl-pyrophosphoryl-*N*-acetylglucosamine	TOF (ATT)	Use of an enzymatic reaction catalyzed by the integral membrane protein, WecA	(Al-Dabbagh et al., 2009)
O-Polysaccharide (chimeric glycopeptide) and peptide mimic from *Shigella flexneri*	TOF (DHB), FAB, LC-MS	Synth. by solution and solid-phase strategies. Immunochemical characterization showed that α-glycopeptide did not inhibit binding	(Hossany et al., 2009)
Repeating unit from *Streptococcus pneumoniae* type 1 capsular PS	Sector-TOF	First synthesis of a hexasaccharide representing two repeating units	(Wu et al., 2010c)
Tetrasaccharide repeat from cell wall teichoic acid from *Streptomyces* sp. VKM Ac-2275	TOF	Chemical synthesis	(Ghosh & Misra, 2009)
Tri- and penta-saccharides from the O-antigen of *Shigella boydii* type 6	MALDI	Chemical synthesis. For experiments on glycoconjugate-based therapy	(Santra & Misra, 2010)
Carbohydrates from fungi			
Mannose hexasaccharide	MALDI, ESI	Related to the cell wall mannan of *Candida dubliniensis* and *Trychophyton mentagrophytes*	(Zong et al., 2010b)
Carbohydrates from nematodes etc.			
Branched tri-, tetra- and pentasaccharides from *Echinococcus multilocularis* antigen	TOF	Branched tri-, tetra- and pentasaccharides displaying a Gal β(1→3)GalNAc core in the glycan portion of the glycoprotein antigen	(Koizumi et al., 2009)
Peptidoglycans			
β-GlcN-(1→4)-MurNAc disaccharide	TOF	As building block for *N*-deacetylated peptidoglycan fragments	(Cirillo et al., 2010a)
Muropeptides from various Gram positive and negative bacteria	TOF	Results show that Toll-like receptor 2 can differentially recognize peptidoglycan from Gram-positive and Gram-negative bacteria	(Asong et al., 2009)
Peptidoglycan precursors, Lipid IIand Lipid IV plus analogues	TOF	With glycan chains of varying length	(Lupoli et al., 2009)
Glycosphingolipids and related glycans			
N-Acetyl-2-amino-2-deoxy-α-D-galactosyl 1-thio-7-oxaceramide	MALDI (DHB)	Synthesis of new analogue of α-D-galactosyl ceramide. Failed to stimulate invariant natural killer T cells	(Rajan et al., 2009)
O-Ac and *O*-Bu derives of neurostatin	R-TOF/TOF (DHB), ESI	Synthesis and characterization. High inhibitory activity of glioma growth	(Valle-Argos et al., 2010)
BODIPY-labelled GM1 gangliosides	TOF	For exploring lipid membrane properties and specific membrane-target interactions	(Mikhalyov et al., 2009)
BODIPY-labelled glyco-sphingolipids	TOF (DHB)	4,4-Di-F-1,3,5,7-tetra-Me-4-bora-3a,4a-diaza-*s*-indacene-8-yl (Me_4-BODIPY-8) group at the ω-position of a fatty acyl residue	(Boldyrev & Molotkovsky, 2010)
α-Gal-Ceramide analog	TOF	Based on the structure of CD1d, with a 4-(4-fluorophenoxy)-Ph undecanoyl modification of the *N*-acyl moiety	(Lin et al., 2010d)
Ganglioside HLG-2 from *Holothuria leucospilota* (sea cucumber)	TOF (CHCA)	Carbohydrate = α-*N*-glycolylsialyl-(2→4)-α-*N*-acetylsialyl-(2→6)-glucoside	(Iwayama et al., 2009)

TABLE 27. (*Continued*)

Gangliosides labelled with (4,4-difluoro-5-styryl-4-bora-3*a*,4*a*-diaza-*s*-indecenyl)-5-pentanoic or -undecanoid acids	TOF	Attachment to N of sphingosine or sialic acid. As probes for membrane studies	(Gretskaya & Mikhalyov, 2009)
Nonsialylated neolacto-based glycosphingolipids	TOF (DHB)	Binding of *Helicobacter pylori* to new glycans based on *N*-acetyllactosamine	(Miller-Podraza et al., 2009)
a-Series ganglioside glycans GT1a, GD1a, GM1	TOF (CHCA)	Synthesis using using the newly developed *N*-Troc-protected GM3 and GalN intermediates	(Komori et al., 2009)
GPI Anchors			
Anchor with N-terminal Cys	MALDI	General method for producing proteins containing a natural GPI anchor using expressed protein ligation	(Schumacher et al., 2010)
Anchor with unsaturated lipid chains	TOF	To investigate mechanism of GPI anchoring	(Swarts & Guo, 2010)
Synthetic glycosides and related compounds			
Acetylated cholesterol galactosides	TOF/TOF (DHB, THAP)	For construction of vaccine against Lyme disease	(Stübs et al., 2010)
Aminoglycosides	TOF	Development of novel aminoglycoside (NB54) with reduced toxicity and enhanced suppression of disease-causing stop mutations	(Nudelman et al., 2009)
Biotin-labeled photoactive mannosides	TOF/TOF (CHCA)	For photoaffinity labelling of bacterial fimbrial lectin FimH	(Lindhorst et al., 2010b)
Biotinylated α-D-Ara*f*-(1→5)-α-D-Ara*f*	MALDI	For development of a plate-based scintillation proximity assay for mycobacterial enzyme involved in cell wall arabinan biosynthesis	(Zhang et al., 2010d)
Biotinylated sialoside	TOF	To probe CD22–ligand interactions	(Abdu-Allah et al., 2009)
5a-Carba-glycopyranoside primers	TOF (DHB)	As building blocks for biocombinatorial synthesis of glycosphingolipid analogues	(Aoyama et al., 2009)
Carbohydrate-functionalized mono- and di-(2,2':6',2''-terpyridinyl)arenes	TOF	For synthesis of self-assembled nanofibers	(Chan et al., 2009c)
Carbohydrate-phthalocyanine conjugates	TOF, ESI	Synthesis by Huisgen or by glycosylation reaction	(Ermeydan et al., 2010)
β,β-Carotene-4,4'-*bis*-thioglucoside	TOF	Mimetics of naturally occurring thermoxanthins. Show favourable effects against oxidation stress	(Nagy et al., 2010)
Cationic cholesteryl glucosides	TOF (DHB), ESI	Containing pyridinium, *N*-Et-imidazolium, *N*-Me-morpholinium, and *N*-Me-piperidinium linked *via* β-glucosyl spacer	(Maslov et al., 2010)
Chiral amphiphilic liquid crystals	TOF	Containing β-D-Gal*p* end-group and 4-[1,2,3]-triazolephenyl 4-alkoxybenzoate mesogens	(Ho & Hsu, 2010)
Dimedone-*C*-glycosides	TOF (DHB)	For electron impact fragmentation studies.	(Adeuya & Price, 2009)
1,2-Distearoyl-sn-glycero-3-phosphoethanolamine-*N*-(polyethylene glycol)-2000 plus sucrose or maltose	TOF (sinapinic)	Preparation of liposomes for targeting anticancer drugs	(Song et al., 2009a)
Di- and tri-mannosylated C_4H_{10} - C_7H_{16}	MALDI	Synthesis and ^{13}C NMR spectroscopy as model compounds for the microstructure analysis of poly(vinyl glycoside)s	(Yuan & Frauenrath, 2009)
L-DOPA-α-glycosides	TOF (DHB)	Reaction of cyclomaltohexaose catalyzed by cyclomaltodextrin glucanyltransferase	(Yoon et al., 2009)
Fatty acyl-glycerol congugates	R-TOF (DHB)	Clickable glycol-lipids containing azido and alkynyl fatty acids and triacylglycerols	(Zerkowski et al., 2009)

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TABLE 27. (*Continued*)

C-Furyl glycosides	TOF (DHB)	Bearing pyrazolines, isoxazolines, and dihydropyrimidine-2(1H)-thiones. As antibiotics	(El-Sayed et al., 2009)
Hydroquinone fructoside	L-TOF	Synthesis using *Leuconostoc mesenteroides* levansucrase	(Kang et al., 2009a)
Hydroquinone glucoside	L-TOF (DHB)	Synthesis using *Leuconostoc mesenteroides* levansucrase	(Seo et al., 2009)
Lobatoside E-related triterpene glycoside	MALDI	Gold(I)-catalyzed glycosylation with glycosyl *ortho*-alkynylbenzoates as donors	(Li et al., 2010g)
Man-α-(1→6)-Man-*O*-Octyl analogues	MALDI	Synthesis and evaluation as potential substrates and inhibitors of a PPM-dependent α-(1→6)-mannosyltransferase involved in LAM/LM biosynthesis	(Tam & Lowary, 2010)
Mannosylated pyrene-perfluoroalkyl lipid	MALDI	To study multivalent binding on the lateral phase separation of adhesive lipids	(Liem et al., 2010)
Mannosyl glycolipids with perfluoroalkyl membrane anchors	MALDI	To assess the cluster glycoside effect during the binding of concanavalin A to mannosylated artificial lipid rafts	(Noble et al., 2009)
Mesogenic azobenzenes tethered to sugar alcohols	R-TOF (CHCA) ESI	For color changes in liquid crystals	(Akiyama et al., 2009)
p-Nitrophenyl T-antigen analogues	TOF (CHCA)	Di-*tert*-butylsilylene-directed α-selective synthesis	(Sato et al., 2009b)
Pentacyclic triterpenes with D-glucose	MALDI	Click chemistry, for homo/heterobivalent inhibition of glycogen phosphorylase	(Cheng et al., 2010b)
Propargyl and *n*-pentenyl glycosides	TOF	Glycosides can be selectively activated with NIS/TMSOTf in the presence of either armed or disarmed propargyl *O*-glycosides.	(Vidadala et al., 2009)
S-Glycooxazolines	TOF (1,8,9-anthracene-triol)	Linked with alkyl chains of varying lengths. Synthesis and ring-opening polymerizations	(Takasu & Kojima, 2010)
Salicin glycosides	TOF	Transglycosylation catalyzed by amylosucrases from *Deinococcus geothermalis* and *Neisseria polysaccharea*	(Jung et al., 2009)
Thiourea-bridged glyco-OEG azides	TOF (DHB, CHCA)	For preparation of self-assembled monolayers by click chemistry	(Grabosch et al., 2010)
2-*O*-Trifluoromethylsulfonyl-D-mannopyranosides	TOF	As precursors for concomitant ^{18}F-labeling and glycosylation by "click" chemistry	(Maschauer & Prante, 2009)
Glycolipids			
Acetylated glucoselipid	TOF (CHCA), GC/MS	Enzymatic synthesis from diacetylated sophoroselipid	(Imura et al., 2010)
BODIPY-FL–Labeled glycosphingolipids	TOF	Patterns of dimer II formation	(Gretskaya & Mikhalyov, 2007)
Cholesterol plus linear glucose	TOF (DHB)	Synthesis and gelling properties	(Gao et al., 2010)
1,2-Dipalmitoyl-3-(*N*-palmitoyl-6'-amino-6'-deoxy-α-D-glucosyl)-sn-glycerol	TOF	Glycoglycerolipid of a marine alga with a high inhibitor activity against human Myt1-kinase. Synthesis starting from α-Me-Glc*p*	(Göllner et al., 2009)
Glucose-based analogues of phosphatidylinositol 3-PO_4	TOF (DHB)	Synthesis from 2,3,4,6-tetra-*O*-acetyl-D-Glc-Br as protein kinase B (PKB/Akt) inhibitors.	(Cipolla et al., 2010)
Glycoglycerophospholipid from *Mycoplasma fermentans*	TOF/TOF (DHB)	Enzymatic synthesis from 1,2-dipalmitoylglycerol in one pot reaction	(Ishida et al., 2010)
Hydroquinone galactosides	L-TOF (DHB)	A potential skin whitening agent. Synthesis by reaction of lactase with lactose as donor.	(Kim et al., 2010a)

TABLE 27. (*Continued*)

Long chain *C*-glycoside ketohydrazones	R-TOF (DHB), GC/MS	Hydrazides from fatty acid methyl esters catalysed by lipase. Used to prepare hydrazones without protection.	(Carpenter et al., 2010)
Man_3 conjugated to dipalmitoylphosphatidyl-ethanolamine	TOF	For induction of Th1 immune responses against antigens entrapped in oligomannose-coated liposomes	(Ishii et al., 2010)
Mannosylerythritol lipids	TOF (CHCA)	Biosurfactant, from *Pseudozyma parantarctica*	(Morita et al., 2009b)
Mannosylerythritol lipids	TOF (CHCA)	Production by smut fungus (*Ustilago scitaminea* NBRC 32730)	(Morita et al., 2009a)
Monoacylated amide-linked disaccharide glycolipids	TOF	Synthesis with saturated and unsaturated acyl groups. Physical properties of aggragates, including phase diagrams.	(Gerber et al., 2009)
Mycobacterium leprae phenolglycolipid-1	TOF	Expressed by genetically engineered *Mycobacterium bovis* BCG	(Tabouret et al., 2010)
Neoglycolipids with dipalmitoyl-phosphatidylethanolamine	TOF	With Man_3, lacto-*N*-tetraose, lacto-*N*-neotetraose, LNFPI, LNFPII and LNFPIII. For production of anti-carbohydrate antibodies by phage display	(Yuasa et al., 2010)
19-*O* esters of steviolobioside from *Stevia rebaundiana*	TOF (CHCA)	Containing benzyl, phenoxyl, and 6-methy-luracyl fragments, Antibacterial	(Sharipova et al., 2009)
PEGylated lactose	TOF	For inhibition studies on *Trypanosoma.cruzi* trans-sialidase	(Giorgi et al., 2010)
Phosphate-linked disaccharide with four tetraethylene glycol tails carrying dansyl units	L-TOF (3,5-DHB)	Fluorescently labelled synthetic ionophore synthesises in 12 steps with 26% yield	(Coppola et al., 2010)
Phosphatidyl-*myo*-inositol mannosides	TOF	To study mannosyltransferase *Corynebacterium glutamicum* PimB'	(Batt et al., 2010)
Puerarin-cycloamylose inclusion complex	L-TOF (DHB)	Enzymatic synthesis using 4-α-glucanotransferase and maltogenic amylase	(Choi et al., 2010)
Sialic acid-containing lipid linker	TOF (DHB)	For construction of gold nanoparticles	(Niikura et al., 2009)
Tri-Ac phosphatidylinositol dimannoside	MALDI	Seven-steps from *myo*-inositol 1,3,5-orthoformate	(Patil & Hung, 2010)
Undecaprenyl pyrophosphate-linked glycans	TOF (DHB), ESI	As donor substrates for bacterial protein *N*-glycosylation	(Lee et al., 2009m)
Cyclodextrins (CDs)			
N-Alkyl pyridinium compounds plus α-CD	TOF (s-DHB)	Form hydrogels in aqueous media	(Taira et al., 2010b)
Amino–acetone-bridged cyclodextrins	TOF (dithranol)	Bridge attached to 6A and 6D positions of α- and β-CDs as artificial alcohol oxidases	(Marinescu et al., 2010)
Bifunctional peptide derivatives	TOF	β-cyclodextrin core. Two CDs linked with peptide for drug delivery	(White et al., 2010)
BODIPY-bridged bis(permethyl-β-CDs	FT-ICR	For synthesis of poly-porphyrin mediated by β-cyclodextrin dimers	(Gu et al., 2010b)
Branched β-cyclodextrins with α-L-Fuc*p*	TOF (DHB), FAB	Synthesis, characterization and function (with fucose-binding lectin)	(Nishi & Tanimoto, 2009)
CD9–CD25	TOF	Separation on a silica-bonded [60]fullerene stationary phase	(Bogdanski et al., 2010)
Cinnamoyl-α-cyclodextrin	TOF	Initiates polymerization of δ-valerolactone	(Osaki et al., 2009)
Cinnamoyl α-cyclodextrin	TOF	CDs self-organize to give different supra-molecular complexes in aqueous solutions	(Tomimasu et al., 2009)

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TABLE 27. (*Continued*)

Cyclodextrin aldehydes	TOF (CHCA)	Found to catalyse oxidation of aminophenols in the presence of hydrogen peroxide	(Fenger et al., 2009)
Cyclodextrin-based hyperbranched polymers	TOF (CHCA)	Synthesized *via* hydrosilylation reaction under thermal or UV- activated polymerization	(Tian et al., 2009)
CD-based telluronic acid plus Mn(III)meso-tetra[1-(1-adamantyl methyl ketone)-4-pyridyl] porphyrin	MALDI	As artificial enzyme with superoxide dismutase and glutathione peroxidase activities	(Yu et al., 2010d)
Cyclodextrin dimers	TOF	One homo-dimer of β-CD and two hetero-dimers of α-CD and β-CD as hydrolases	(Ikeda et al., 2010)
Cyclodextrin dimers and trimers	TOF/TOF, ESI	Bridged CDs with links at different positions formed supramolecular adducts with shape-specific ligands	(Aime et al., 2009)
β-Cyclodextrin cyclic-nitrone conjugate	MALDI	With superoxide radical anion and dodecyl chain for membrane insertion	(Han et al., 2009)
α-, β- and γ-Cyclodextrin-esters (acrylate, pent-4-enoate and undec-10-enoate)	TOF (CHCA)	Synthesis with nitrophenol esters	(Nielsen et al., 2010a)
β-CD plus hydroquinone-α-glycoside	TOF	Synthesis and doxorubicin-inclusion abilities	(Oda et al., 2009)
β-CD monoalkyn	TOF (DHB)	For conjugation to long-chain thiols for self-assembled monolayer prep.	(Dubacheva et al., 2010)
Cyclodextrin-polyester polymers	TOF	Ring-opening polymerization - heating cyclic esters and CDs	(Harada, 2009)
γ-CDs possessing an azido group and a triisopropyl-benzenesulfonyl group	TOF (DHB)	As useful synthetic and authentic intermediates for unsymmetrically functionalized derivatives	(Himeno et al., 2009)
β-CD-ended linear poly(*N*-isopropylacrylamide) (β-CD-PNIPAM)	TOF (THAP, DCTB)	Self-assembly of PNIPAM-based amphiphiles formed by inclusion complexation	(Zou et al., 2009)
β-CD with octadecyl-linked perylene bisimide	MALDI	Self-assembled amphiphilic perylene-CD conjugate for vapor sensing of organic amines	(Jiang et al., 2010a)
[6-Deoxy-6-(1-H-1,2,3-triazol-4-yl)(Me)6-(4-OMe-bi-Ph-4'-yloxy) hexanoyl]-β-cyclodextrin	TOF (DHB)	Synthesis, liquid-crystalline properties, and supramolecular organization	(Chen et al., 2010a)
7^{A},7^{D}-Dicyanohydrin-β-cyclodextrin	TOF (DHB)	Glycosidase enzyme mimic that catalyzes hydrolysis of aryl glycosides with up to 5500 times rate increase	(Bjerre & Bols, 2010)
Di-phenylphosphane-linked β-CD	TOF (DHB)	Exhibits solubility in water and organic solvents. Has solvent-tuneable conformation that affects catalytic properties	(Machut-Binkowski et al., 2010)
DNA-β-CD conjugates	TOF	Synthesis and hybridization of two types of conjugate	(Kuzuya et al., 2009)
Estradiol–cyclodextrin conjugates	TOF (DHB)	Click synthesis. As drug carrier	(Kim et al., 2010b)
Ferrocene–β-cyclodextrin conjugates	TOF (CHCA)	Synth. by regiospecific copper(I)-catalyzed cycloaddition of 2-*O*-propargyl-β-CD to azidoMe or bis(azidoMe) ferrocene. As electrochemical sensor	(Casas-Solvas et al., 2009a)
Ferrocene–β-cyclodextrin conjugates	L-TOF/TOF (DHB)	Compounds self-organize to cyclic supramolecular structures	(Munteanu et al., 2010)
Hydrophobic β-cyclodextrin polymers	TOF (CHCA)	Polymers with styrene, allylbenzene and 4-phenyl-1-butene	(Nielsen et al., 2009)

TABLE 27. (*Continued*)

Hydroxypropyl-substituted β-CD:steroid complexes	TOF (CHCA)	Influence of the degree of substitution on thermodynamics of complexation	(Schönbeck et al., 2010)
Inclusion complexes of γ-CD and carboxyl-modified γ-CD with C_{60}	TOF (CHCA)	Used as microgel solvent (or swelling agent) for controlled release application.	(Adrian et al., 2009)
Inclusion complexes of β-CD with bipyridine guests	TOF	With 4,4'-vinyl-enedipyridine, 2,2'-vinylenedipyridine, 1-(2-pyridyl)-2-(4-pyridyl)ethylene, 4,4'-ethylene-dipyridine, 4,4'-dithiodipyridine, and 2,2'-dithiodipyridine	(Zhao et al., 2009c)
Insulated molecular wire with highly conductive π-conjugated polymer core	TOF	Rod-like -Ph-C≡C-Ph- core coated with α-CDs	(Terao et al., 2009b)
Ionic-liquid-functionalized β-cyclodextrin	TOF	As bonded chiral stationary phases for HPLC	(Zhou et al., 2010b)
Linear α-cyclodextrin oligomers	TOF	Controlled synthesis using copper-catalyzed Huisgen 1,3-dipolar cycloaddition	(Rawal et al., 2010)
Oligothiophene derivatives bearing β-cyclodextrin	TOF (DHB)	2T-β-CD_2 and 3T-β-CD_2, with bithiophene and terthiophene with β-CD at each end form supramolecular assemblies in aqueous solns.	(Sakamoto et al., 2009b)
Perylene bisimide-bridged *bis*-(permethyl-β-CDs)	FT-ICR	As solid-state fluorescence sensor for vapor detection	(Liu et al., 2009i)
Perylene-bridged *bis*(β-cyclodextrin)	FT-ICR	Molecular aggregation behavior and electronic interactions upon selective binding with aromatic guests	(Wang et al., 2010a)
Porphyrin-cyclodextrin conjugates	TOF	As nanosystem for drug delivery and multimodal cancer therapy	(Králová et al., 2010)
Pyrene-β-cyclodextrin dimer	TOF	Forms supramolecular associations in aqueous media	(Ogoshi et al., 2010)
Quinolinocyclodextrin plus porphyrin	TOF	Synthesis and transmembrane dissociation behaviour	(Yu et al., 2010b)
Vinylbenzene and hexanoate-derivatized β-CD	TOF	For use in adhesion-promoting monomer formulations for dental applications	(Bowen et al., 2009)
Rotaxanes			
Cyclodextrin pseudorotaxanes.	TOF	For synthesis of thermosensitive hydrogels	(Taira et al., 2009a)
Encapsulated amino-azobenzene dye rotaxanes	TOF	With *N*,*N*-dimethylamino end groups and α-cyclodextrins	(Park & Koh, 2009)
Light-switchable janus [2]rotaxanes	TOF	With α-CD and bearing two recognition sites linked with oligo(ethylene glycol)	(Li et al., 2010e)
Multivalent carbohydrate ligands from pseudo-rotaxanes	TOF/TOF	Synthesised by assembling lactosyl-α-cyclodextrin-based pseudo-rotaxanes through "click" chemistry	(Chwalek et al., 2009)
Polyrotaxane	QIT-TOF (DHB)	Organic-soluble conjugated polyrotaxanes. Synth. by polymerization of linked rotaxanes	(Terao et al., 2009a)
Polyrotaxane composed of γ-CD and single poly(ethyelene glycol) chain	TOF	Loose-fit polyrotaxane. Making room in γ-CD cavity for additional inclusion complexation	(Takahashi et al., 2009)
Pseudo[1]rotaxane dimer	TOF	Synthesis from an *altro*-α-CD by tumbling in D_2O	(Yamauchi et al., 2010a)
[2] and [3]Rotaxanes	TOF	Synthesis of molecule with part (CD) capable of shuttling	(Yamauchi et al., 2010b)
Rotaxanes of α-CD capped by 1-adamantaneacetic acid and a deoxyribonucleotide	TOF	For study of the thermodynamic parameters of the dethreading process	(Kuzuya et al., 2010)

(*Continued*)

TABLE 27. (*Continued*)

Polymers			
Aliphatic polyester	TOF	By ring-opening polymerization of a carbohydrate lactone	(Tang et al., 2009b)
Amphiphilic block copolymers based on cyclodextrin host–guest complexes	TOF	*Via* RAFT polymerization of randomly Me-β-CD-complexed hydrophobic acrylamide and hydrophilic *N*,*N*'-di-Me-acrylamide from homogeneous solution	(Köllisch et al., 2009)
7- and 21-Arm Poly(*N*-sopropyl-acrylamide) star polymers with β-CD cores	TOF (DHB)	Synthesis *via* click chemistry and their thermal phase transition behaviour in aqueous solution	(Xu & Liu, 2009)
Biotin chain-end functionalized boronic acid-containing polymer	TOF	As functional glyco-affinity macroligand	(Chalagalla & Sun, 2010)
Carboxylic acid-functionalized glycopolymers	L-TOF (DHB)	Synthesised *via* one-step postpolymerization modification of poly(*N*-[3-aminopropyl] methacrylamide)	(Alidedeoglu et al., 2010)
Dithiolated poly(2-methacryloyloxyethyl D-mannopyranoside	TOF	For kinetic study on the binding of lectin to mannose residues	(Kitano et al., 2009)
Glycodynamers	MALDI	Dynamic polymers bearing oligosaccharide residues such as Glc_6 obtained from α-CD	(Ruff et al., 2010)
Membranes (cross-linked)	TOF (DHB)	Based on acrylated cyclodextrins and polyethylene glycol dimethacrylates	(Rölling et al., 2010)
Multivalent *Galacto*-trehaloses	TOF	α,β-GT isomers converted into vinyl monomers then radical copoly-merization with 4-acrylamidophemyl-β-Glc or β-GlcNAc) with acrylamide	(Miyachi et al., 2009b)
Pentafluorostyrene copolymers with glucose	TOF	Synthesis by nitroxide-mediated polymerization and "click" chemistry	(Becer et al., 2009)
Polydioxanone with a protected monosaccharide end-group	L-TOF (dithranol)	Ring opening polymerization of *p*-dioxanone using a protected monosaccharide (1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranose) /$Al(OiPr)_3$ initiator system	(Sugih et al., 2009)
Polyfluorene derivative with 20 mol% 2,1,3-benzothiadiazole plus α-Man	R-TOF/TOF (DHB)	Synthesis and characterization of water-soluble conjugated glycopolymer for fluorescent sensing of concanavalin A	(Shi et al., 2010)
Polyhydroxy [n]-polyurethanes	TOF	Prepared from D-galactono-1,4-lactone by a three-step route	(Gómez & Varela, 2009)
Polymer gels from methacrylic functionalized chitooligosaccharides	TOF (DHB)	As injectable material. Cross-linked gel was degradable and nontoxic, with an interesting cytokinetic effect	(Boesel et al., 2009)
Poly(methyl methacrylate) with cellulose side chains	TOF/TOF (DHB)	A cellulose macromonomer, with number averaged DP of 13. Copolymerized with Me-methacrylate to give cellulosic copolymer	(Enomoto-Rogers et al., 2009)
Polyurethanes modified with yucca starch glycoside	TOF	Preparation and properties	(Valero et al., 2009)
Poly(*N*-vinylpyrrolidone) with covalently attached cyclodextrin	TOF (2,4-DHB)	Synthesis by Huisgen reaction. Study of complexation behaviour with phenolphthalein	(Trellenkamp & Ritter, 2010)
Sialic acid-glutamic acid hybrid foldamers	TOF	Most stable foldamer was composed of 6 residues	(Saludes et al., 2009)
Transparent xyloglucan–chitosan complex hydrogels	TOF (DHB)	Xyloglycan oxidized with periodate (MALDI-TOF). Products condensed with chitosan	(Simi & Abraham, 2010b)

TABLE 27. (*Continued*)

α,α-Trehalose-based polyacetals and macrocyclic acetals	TOF (DHB)	The polycondensation of 1,x-bis(2-formylphenoxy)alkanes with α,α-trehalose using acidic catalyst	(Kukowka & Maślińska-Solich, 2010)
Antibiotics and other drugs			
Amphiphilic neamine derivatives	TOF (DHB)	One to four hydroxyl functions capped with phenyl, naphthyl, pyridyl, or quinolyl rings. antimicrobial evaluation	(Baussanne et al., 2010)
Amphotericin B arabinogalactan conjugate	MALDI	To increase solubility	(Elgart et al., 2010)
Des-tallose-tallysomycins	FT-MS, ESI	Study of tallysomycin biosynthesis and production of novel bleomycin analog	(Tao et al., 2010)
28,29-Didehydronystatin A1 derivatives	TOF/TOF	23 Derivatives by modification of C16 group and amino group of sugar. Anti-fungal.	(Preobrazhenskaya et al., 2009)
Fluoroquinolone-aminoglycoside hybrid antibiotics	TOF	Fluoroquinolone (ciprofloxacin) and aminoglycoside (neomycin) antibiotics linked *via* 1,2,3-triazole moiety	(Pokrovskaya et al., 2009)
Glycosylated chlorambucil	FT-ICR, ESI	Assessment of chemoselective neoglycosylation methods	(Goff & Thorson, 2010)
LacdiNAc-terminated glycoconjugates	TOF (DHB)	Synthesis by mutant galactosyltransferase	(Bojarová et al., 2009)
6-Morphinyl-α-D-mannopyranoside	TOF, ESI	Naloxone-reversible antinociception. 100-Fold more potent and lasts twice as long as morphine	(Arsequell et al., 2009)
Neomycin-Hoechst 33258-pyrene conjugate	TOF	To study binding to B-DNA	(Willis & Arya, 2010)
Olivomycin 1, 5-aryldiazenyl-6-*O*-deglycosyl derivatives	TOF, ESI	Reaction with aryl diazonium salts	(Tevyashova et al., 2009)
Pregabalin derivatives	TOF/TOF	Synthesis and activity in gabapentin receptor binding assay	(Horvat et al., 2010)
Pseudo-di- and pseudo-trisaccharide derive. of the aminoglycoside drug G418	TOF	Development of new derivatives of geneticin (G418) with enhanced suppression of diseases-causing nonsense mutations	(Nudelman et al., 2010)
L-Rhamnose-containing three-component vaccine	TOF/TOF	Synthesis and evaluation of antigenicity in the presence of anti-L-rhamnose antibodies	(Sarkar et al., 2010)
S- and *C*(*1*)-Substituted analogues of lincomycin	MALDI (DHB)	Synthesis of new thioglycosides and *C*(*1*)-alkylated thioglycosides (*S*-ulosides)	(Collin et al., 2009)
Teicoplanin and ristocetin aglycon derivatives	TOF	Click chemistry. High antibacterial and anti-influenza virus activity	(Pintér et al., 2009)
TMG-chitotriomycin	MALDI	Total synthesis and structural revision	(Yang et al., 2009b)
Vancomycin derivatives with acrylamide or PEG-acrylate	TOF (HABA)	For bactericidal biomaterial surface modification	(Lawson et al., 2009)
Microarrays, Nanoparticles			
2-Amino-*N*-(2-aminoethyl)-benzamide (AEAB) fluorescent derivatives	TOF/TOF	Synthesis of fluorescent derivatives of glycans, construction of microarray and use for detecting galectin ligands	(Song, et al., 2009d)
High-mannose-gold nanoparticles	TOF/TOF (DHB)	To increase binding to DC-SIGN on dendritic cells. Anti-viral treatment for HIV by mimicking mannose patch on gp-120	(Martínez-Ávila et al., 2009)
MUC1 Glycopeptides	TOF	On an amine-reactive hydrogel-coated microarray glass surface. To detect autoantibodies in breast cancer	(Blixt, et al., 2010) Correction: (Blixt, et al., 2011)
Nanofibres	TOF	Nanofibers formed through π· · ·π stacking of the complexes of glucosyl-*C*2-salicyl-imine and phenylalanine	(Acharya et al., 2010)

(*Continued*)

TABLE 27. (*Continued*)

Neu5Ac-Gal-functionalized gold glyconanoparticles	TOF (CHCA)	For study of carbohydrate-protein interaction	(Zhang et al., 2009c)
Oligosaccharides from plants	TOF (DHB)	For construction of microarray to screen for plant transglycosidases activity	(Kosík, et al., 2010)
6-sulfo-*N*-acetyl-D-glucosamine containing, on gold	TOF	To study mechanism of amyloidosis of amyloid β peptides	(Fukuda et al., 2010b)
Miscellaneous			
β-D-Allopyranoside-grafted Ru(II) complex	TOF	Synthesis and both acid-base and DNA-binding properties	(Ma et al., 2009)
Azo-sugar nucleotides plus many alkynes	TOF (DHB)	Click chemistry (Huisgen reaction) to produce inhibitors of glycosyltransferases	(Hosoguchi et al., 2010)
1-Deoxy-1-nitropiperidinoses	MALDI	Synthesis from a protected galacto-octopyranose	(Collin & Vasella, 2010)
4,4-Di-F-5,7-di-Me-4-bora-3a,4a-diaza-sindacene-3-propionic acid derivative of $Man_5GlcNAc_2$. (BODIPY)	TOF	For development of fluorescence assay	(Haga et al., 2009)
Carbohydrate-functionalized salphen–metal complexes	TOF	Complexes with peripheral glucose and galactose substituents. Self-assembled supramolecular structures were produced	(Hui et al., 2009)
Dioxolane-type (9'-anthracenyl)methylene acetals	TOF	Synthesis, regioselective hydrogenolysis, partial hydrogenation, conformational study	(Jakab et al., 2009)
Glucopyranoside-incorporated *N*-heterocyclic carbene complexes	TOF	Complexes of silver(I) and palladium(II). Efficient water-soluble Suzuki-Miyaura coupling palladium(II) catalysts	(Yang et al., 2010b)
1-(D-Glucopyranosyl-2'-deoxy-2'-iminomethyl)-2-hydroxybenzene	TOF	As chemosensor for aromatic amino acids by switch-on fluorescence. MALDI to check stoichiometry of complex with Trp and Phe	(Mitra et al., 2010)
Fluorescently labeled glucose-DNA conjugates	TOF (THAP)	Synthesis, cell-surface binding, and cellular uptake	(Ugarte-Uribe et al., 2010)
Ibuprofen-modified xylan	TOF	MALDI-TOF to characterize xylan	(Daus & Heinze, 2010)
Mannostatin A analogues	TOF	Investigation of the molecular basis of inhibition of Golgi α-mannosidase II by mannostatin A	(Kuntz et al., 2009), corrigendum (Kuntz et al., 2009)
Novel *gluco*- and *galacto*-functionalized platinum complexes	TOF (DHB), FAB, ESI	Active as anti-cancer drugs	(Möker & Thiem, 2009)
Oligonucleotide conjugates with Man or Gal core bearing four Gal residues	TOF	Synthesised by phosphoramidite chemistry and copper catalyzed azide alkyne 1,3-dipolar cycloaddition	(Pourceau et al., 2010)
Oligosaccharides tagged with peptide nucleic acids	MALDI	For mimicking carbohydrate epitope of HIV	(Gorska et al., 2009)
Phosphate-linked 12-membered disaccharide ring, fused to two 18-crown-6 ether residues	TOF (DHB)	23% overall yield for 11 reaction steps, exploiting phosphoramidite chemistry for the dimerization and a classical phosphotriester methodology for the cyclization reaction	(Coppola et al., 2009)
Self-assembling carbohydrate-functionalized oligothiophenes	TOF (dithranol, DHB)	Synthesis by mild Sonogashira cross-coupling conditions	(Schmid et al., 2009)
Supermolecular tetrapedes	TOF	Core = Me-α-D-Glc*p* or Me-α-D-Man*p* attached with C6 or C11 alkyl chains to four cyanobiphenyl mesogenic groups	(Belaissaoui et al., 2010)
Triazole-substituted *O*-galactosyl aldoximes	TOF, FAB, ESI	50 Compounds. Some had high-affinity inhibitors of galectin-3	(Tejler et al., 2009)

[1]Format (not all items present): MALDI method (matrix), derivative. "MALDI" is used when the instrument is not specified.

TABLE 28. Use of MALDI MS for Monitoring Products of the Synthesis of Glycosides

Compound (source)	Glycans	Methods[1]	Notes	Reference
Anemarrhena asphodeloides Bunge (Liliaceae)	Timosaponin BII from rhizomes	TOF (CHCA), NMR	Synth. in 10 steps, 18% yield. Evaluated against HL-60 human promyelocytic leukaemia cells.	(Cheng et al., 2009)
Anemone flaccida Fr. Schmidt	Oleanolic acid saponins (from dry rhizome)	TOF (CHCA)	Synthesis of oleanolic acid saponins mimicking components of Chinese folk medicine Di Wu	(Huang et al., 2009c)
Dioscin	Diosgenyl saponins	MALDI, ESI	Synthesis of analogues with aromatic nitro groups	(Kaskiw et al., 2009)
Flaccidoside II	Triterpene saponin	TOF	From Di Wu, a Chinese folk medicine from dry rhizome of *Anemone flaccida* Fr. Schmidt	(Liu et al., 2009c)
Kitasatospora kifunensis MJM341	Isoflavonoid glycosides	MALDI	Chemical synthesis of Talosin A and B	(Wu et al., 2010g)
Mangiferin indica L.	Mangiferin, isomangiferin, homomangiferin	MALDI	*C*-Linked tetrahydroxy-xanthones. Synthesised with per-Bz-Glc*p N*-Ph-trifluoroacetimidate	(Wu et al., 2010e)
Mycoplasma pneumoniae	β-Glyceroglycolipid antigens	TOF	First stereoselective synthesis	(Miyachi et al., 2009a)
Quillaja saponaria Molina	Cationic derivatives of Quil A	TOF (HPA)	Synthesis of cationic immune-stimulating complexes	(Pham et al., 2009)
Palhinhaea cernua (club moss)	Apigenin-4'-yl 2-*O*-(*p*-coumaroyl)-β-D-glucopyranoside	TOF (CHCA)	Synthesis in seven steps from a 1,2-blocked sugar unit and natural apigenin	(Zhang et al., 2010e)
Picea obovata Ledeb, *Stenochlaena palustris, Pinus sylvestris* L.	Kaempferol 3-*O*-(3'',6''-Di-*O*-*E*-*p*-coumaroyl)-β-D-glucopyranoside	MALDI	Efficient glycosylation of flavonol 3-OH with glycosyl *o*-alkynylbenzoates as donors	(Yang et al., 2010g)
Plakortis simplex (Caribbean sponge)	Plakosides	MALDI	Concise synthesis of two natural triterpenoid saponins, oleanolic acid derivatives isolated from roots	(Lü et al., 2009)
Pseudopterogorgia elisabethae (sea whip)	Pseudopterosin analogues	MALDI-FT-MS	Synthesis and *in vivo* anti-inflammatory activity	(Flachsmann et al., 2010)
Pulsatilla chinensis	Triterpenoid saponins, oleanolic acid derivatives from roots	MALDI	Use of odourless 2-methyl-5-*tert*-butylphenyl thioglycoside and trichloroacetimidate donors in one-pot reaction as a key step	(Liu et al., 2009d)
Ranunculus sieboldii	7-*O*-β-D-Glucopyranosyl-4'-*O*-α-L-Rha*p* apigenin	MALDI (DHB)	Synth. in six steps, 20% yield from apigenin. good anti-hepatitis B virus and anti-stroke activities	(Gao et al., 2009a)
Sacbiosa tschiliensis Grun. (Dipsacaceae)	Oleanolic acid saponins	MALDI	From Chinese traditional medicine Synth. by one-pot strategy with glycosyl trichloroacetimidates and *p*-toluene-1-thioglycosides	(Guo et al., 2009a)
Salvia Patens	*Bis*-glycosyl apigenin	MALDI (DHB)	Synthesis in only four steps from naringenin	(Chen et al., 2009a)
General	3-*O*-β-Chacotrioside and chlorogenin 6-α-*O*-actyl-3-*O*-β-chacotrioside	MALDI	Discovery of the first series of small molecule H5N1 entry inhibitors	(Song et al., 2009b)

[1]Format (not all items present): MALDI method (matrix). "MALDI" used when instrument not specified.

TABLE 29. Use of MALDI MS to Study Methods for General Synthesis

Compound	Methods[1]	Method/notes	Reference
Alkyl glycosides	L-TOF (DHB)	Synthesised with *Leuconostoc mesenteroides* dextransucrase	(Kim et al., 2009f)
Amino-sugars	TOF (CHCA), ESI	Deprotection method for the 2,2,2-trichloroethoxycarbonyl (Troc) group using tetrabutylammonium fluoride	(Huang et al., 2010a)
1,6-Anhydro-saccharides	TOF	Use of 7 mol % of AuBr3 to catalyse glycosylations of 6-OH-propargyl/Me mono-, di- and tri-saccharides	(Thadke & Hotha, 2010)
Colored carbohydrates	TOF	Addition of a Fmoc analogue protecting group based on guaiazulene	(Aumüller & Lindhorst, 2009)
4,6-Dialkoxy-1,3,5-triazin-2-yl β-lactosides	TOF (DHB, ESI	Use of novel dialkoxytriazine-type glycosyl donors for cellulase-catalysed lactosylation	(Tanaka et al., 2010d)
2',3'-Dideoxy-aminoglycosides	MALDI	*Via* allylic azide rearrangement	(Zhang et al., 2010c)
Fructose oligosaccharide-lauryl esters	TOF	Molecular sieve found to catalyse acylation of fructose oligomers using vinyl laurate	(ter Haar et al., 2010b)
General carbohydrate	TOF	Use of a practical heavy fluorous tag bound to a benzylic linker	(Goto & Mizuno, 2010)
Glucosamine building blocks for heparin glycans	TOF, ESI	Evaluation of differentially protected GlcN building blocks	(Bindschädler et al., 2009)
Glycoamino acid building blocks	TOF	Use of Staudinger ligation	(Schierholt et al., 2009)
Glycopeptides	TOF	Use of pyruvoyl as a novel protecting group for solid-phase synthesis	(Katayam et al., 2009)
GPI-Anchored proteins	TOF	Sortase A-catalyzed transpeptidation of GPI derivatives for chemoenzymatic synthesis	(Wu et al., 2010f)
Heptasaccharide asparagine building block	TOF (DHB)	Use of one-pot catalytic glycosidation/Fmoc removal	(Mezzato & Unverzagt, 2010)
Homolinear α(1→6)-linked octamannosyl thioglycosides	MALDI	Imidazolium cation-tagged mannosyl fluoride and thiomannoside using block couplings. Efficient alternate approach for oligosaccharide synthesis	(Yerneni et al., 2009)
Homo-oligosaccharides	TOF (DHB) (per-Ac, per-Me)	Base-promoted glycosylation of unprotected glycosyl fluorides	(Steinmann et al., 2010)
Lipophilic thioglycosides	TOF	Use of heavy lipophilic tag to assist biphasic liquid-liquid separation	(Encinas & Chiara, 2009)
Macrocyclic neoglycoconjugates	TOF (CHCA)	Macrocyclization of linear D-galacto-2-heptulopyranose-containing oligoketosides by intramolecular glycosidation and ring-closing metathesis	(Dondoni & Marra, 2009)
Mucin-type *O*-glycopeptides and oligosaccharides	TOF (DHB, THAP, CHCA)	Using transglycosylation and reverse-hydrolysis activities of *Bifidobacterium* endo-α-*N*-acetylgalactosaminidase	(Ashida et al., 2010)
Neu5Gc-containing glycans	TOF	Sialylation with *N*-glycolylneuraminyl phosphite	(Hanashima et al., 2009)
N-linked glycopeptides	TOF	Condensation of glycosylamines with Asn. Demonstrated with $Man_8GlcNAc_2$.	(Chen & Tolbert, 2010)

TABLE 29. (*Continued*)

N-Linked glycoproteins	TOF (for released glycans)	Use of genetic engineering to produce glycoproteins in *E. coli* which are then enzymatically remodelled (see text)	(Schwarz, et al., 2010)
O-Sulfated trisaccharyl glycopeptide	TOF (DHB)	Solid-phase synthesis. Use of new benzyl protection method.	(Kawahira et al., 2009)
Oligosaccharides	TOF (DHB)	Rate acceleration on stereoselectivity and velocity of *O*-glycosylation reactions	(Ishiwata et al., 2010)
Pseudo-oligosaccharides	MALDI	Use of cross-metathesis reaction between sugar-olefins, followed by intramolecular cyclization	(Ronchi et al., 2009)
S-Linked glycoconjugates	TOF, ESI	By-thiyl glycosylation of olefinic proteins	(Floyd et al., 2009)
Sialylated glycans	TOF	Use of Koenigs-Knorr reaction (with Ag_2CO_3)	(Pazynina et al., 2010)
Thioglycosides	R-TOF/TOF	Solvent-free synthesis by use of ball-milling	(Patil & Kartha, 2009)
Trisaccharide libraries	TOF	Use of linker-tagged building blocks imobilized on a soluble polymeric support	(Elsayed, 2009)

[1]Format (not all items present): MALDI method (matrix). "MALDI" used when instrument not specified.

measurement and structure, particularly when structures are selected directly from databases. At present, no one mass spectrometric technique can identify all structural features of carbohydrates. Sialylated and sulfated glycans still remain a problem although sialylated glycans can be handled after suitable derivatization, particularly by permethylation or simply by methyl ester formation. Permethylation appears to be becoming more popular, particularly for quantification and MALDI. The next few years are expected to bring many developments, particularly in instrumentation and ionization techniques, that will possibly address some of the problems with carbohydrate analysis highlighted above.

XVIII. ABBREVIATIONS

2-AB	2-aminobenzamide
2-AA	3-aminobenzoic acid
9-AA	9-aminoacridine
ABOE	aminobenzoic acid octyl ester
AEAB	2-amino-*N*-(2-aminoethyl)-benzamide
AGE	advanced glycation end products
AGP	α1-acid glycoprotein
AlPcs	aluminum-phthalocyanines
α-TF	α-Thomsen–Freidenreich antigen
All	allose
AMAC	aminoacridone
AMT	5-amino-2-mercapto-1,3,4-thiadiazole
ANN	artificial neural networks
ANP	2-amino-5-nitro-4-picoline
ANSA	5-amino-2-naphthalenesulfonic acid
2-AP	2-aminopyridine
APB	aminophenylboronic
APCI	atmospheric pressure chemical ionization
Api	apiose
APTS	8-aminopyrene-1,3,6-trisulphonic acid
AQ	aminoquinoline (3- or 5-)
aoGNP	aminooxy-functionalized gold nanoparticle
Ara	arabinose
Ara4N	4-amino-4-deoxy-L-arabinopyranose
Arg	arginine
Asp	aspartic acid
Asn	asparagine
ATP	adenosine triphosphate
ATT	6-azo-2-thiothymine
AuNPs	gold nanoparticles
Bac	bacillosamine (2,4-diamino-2,4,6-trideoxy-D-glucose)
BACH	biotinamidocaproyl hydrazide
BCG	Bacillus Calmette–Guérin
BEMAD	β-elimination and Michael addition
BHK	baby hamster kidney
BLAC	boronic acid lectin affinity chromatography
BMOSF	boronic acid macroporous silica foam
BMP	windows bitmap
BOA(F)	*O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride
BODIPY	4,4-difluoro-3a,4a-diaza-*s*-indacene
BSA	bovine serum albumin
BSM	bovine submaxillary mucin
BSSL	bile salt-stimulated lipase
bTSH	bovine thyroid-stimulating hormone
CD	cyclodextrin or circular dichroism or nomenclature for cell-surface molecules
CDG	congenital disorder of glycosylation
CE	capillary electrophoresis
CEACAM	carcinoembryonic antigen-related cell adhesion molecule
Cer	ceramide
CF	core fucosylated
CFG	consortium for functional glycomics
CFR	curved-field reflectron
CGE	capillary gel electrophoresis

TABLE 30. Use of MALDI MS to Study Carbohydrate Reactions

Reaction	Methods[1]	Reference
Acceptor specificity in transglycosylation reactions using Endo-M	L-TOF (DHB), ESI	(Tomabechi et al., 2010b)
Acetolysis of 6-deoxyhexosemethyl glycosides. Role of sugar configuration	TOF (DHB)	(Cirillo et al., 2009)
Acid-catalyzed hydrolysis of β-1,4-glucan, including cellobiose and crystalline cellulose with SO_3H-bearing amorphous carbon	TOF	(Suganuma et al., 2010)
Allyloxycarbonyl group removal provides a practical orthogonal protective strategy for carbohydrates	TOF	(Zong et al., 2009)
Amadori ketoses synthesis in microwave field *via* Mo^{VI}-catalyzed stereo-specific isomerization of 2-*C*-branched sugars bearing azido function	TOF	(Hricovíniová, 2010)
Chemoselective glycosylation of carboxylic acid with glycosyl ortho-hexynylbenzoates as donors	MALDI	(Yang et al., 2010h)
Functionalized *C*-glycoside ketohydrazones as derivatives that retain the ring integrity of the terminal reducing sugar	R-TOF (DHB)	(Price et al., 2010b)
β-Glycosidation of sterically hindered alcohols. 2-Chloro-2-Me-propanoic ester acts as a steering group in the Schmidt glycosidation reaction	MALDI	(Szpilman & Carreira, 2009)
Glycosylation of thioglycosides. Use of imidazolium-based ionic liquids as glycosylation promotors	TOF (DHB)	(Galan et al., 2010)
Gold-catalysed glycosylations. Oxophilic $AuBr_3$ cleaves interglycosidic bond of armed disaccharide to to give disaccharide and 1,6-anhydro sugar	TOF	(Kayastha & Hotha, 2010)
Grignard reaction of cyclodextrin-6-aldehydes	TOF (dithranol)	(Lindbäck et al., 2010)
Iodine-hexamethyldisilane mediated anomerization of peracetylated 1,2-*trans*-linked alkyl and aryl glycosides	TOF/TOF	(Malik et al., 2010a)
Iodine–sodium cyanoborohydride-mediated reductive ring opening of 4,6-*O*-benzylidene acetals of hexopyranosides	TOF/TOF	(Rao et al., 2010)
Microwave enhanced stereospecific Mo(VI)-catalyzed transformation of deoxysugars. Stereospecific isomerization of 5-, 6-, and 7-deoxysugars	TOF	(Hricovíniová, 2009)
Oxidation of primary hydroxyl group of Gal in Gal-ceramide with *o*-iodoxybenzoic acid	TOF (DHB)	(Yonekawa et al., 2009)
Ph-boronation of Me-β-D-cellobioside. Investigation of the reaction with different amounts of boronic acid	R-TOF (DHB)	(Meiland et al., 2010)
Phosphorylase-catalyzed *N*-formyl-α-glucosaminylation of maltooligosaccharides	TOF (DHB)	(Kawazoe et al., 2010)
Polymerization of β-Glc*p*-(1→4)-GlcpNAc oxazoline. Revisit to enzymatic transglycosylation by endo-β-*N*-acetylglucosaminidase	TOF/TOF (DHB)	(Ochiai et al., 2009)
Reductive amination for synthesis of unnatural xylan-based polysaccharides	TOF/TOF (DHB)	(Daus et al., 2010)
Selective benzylation and *p*-methoxybenzylation of carbohydrate derivatives in high yields using Ag_2CO_3 as the promoter	TOF	(Malik et al., 2010b)
Selective monofunctionalition of cyclodextrin diols. Regioselective nucleophilic opening of cyclic sulfates. Only one product is formed.	TOF (CHCA)	(Petrillo et al., 2009)
Solvolytic depolymerization of chondroitin and dermatan sulfates. With *o*-iodoxybenzoic acid. Precursors for the synthesis of labeled conjugates	L-, R-TOF (CHCA)	(Toida et al., 2009)
Solid-phase random glycosylation. For glycan libraries. I -*via* Wang esters, II- with polymer-linked donors	TOF (DHB)	(Ágoston et al., 2009a)
Sortase-catalyzed peptide-glycosylphosphatidylinositol analogue ligation	TOF	(Guo et al., 2009b)
Ultrasonically induced depolymerization of chitosan. Shown to involve two mechanisms	TOF (DHB)	(Popa-Nita et al., 2009)
Use of mutated α1,3-Gal-transferase to add C2-modified Gal with chemical handle to LacNAc	TOF (DHB/di-Me-aniline)	(Pasek et al., 2009)

[1]Format (not all items present): MALDI method (matrix). "MALDI" used when instrument not specified.

TABLE 31. Use of MALDI MS for Studies on Glycodendrimers and Glycoclusters

Compound	Methods[1]	Notes	Reference
Alkynyl-terminated scaffold. 1-, 2-, 3-generation dendrimers with 27, 81 or 243 xylose residues	TOF	Use of "click" chemistry. MALDI mass of 27 residue dendrimer (13,801 Da)	(Camponovo et al., 2009)
Benzhydrylamine-lysine capped with 2 to 64 mono-, di- and tri-α-D-Man*p* residues	TOF	Reactive *N*-OH-succinimide esters to ensure complete reaction of dendrimer amines (G3 mass = 13,841 Da)	(Greatrex et al., 2009)
4,7-Bis(9,9-bis(2-(2-(2-azidoethoxy)-ethoxy)ethyl)-fluorenyl)benzo-thiadiazole with 4 mannose residues	TOF (DHB)	As an intelligent energy transfer pair for label-free visual detection of concanavalin A	(Pu et al., 2010)
Boltorn h30 (commercial polymer) with 27 Gal-Cer groups	TOF	Binds HIV-1 gp120	(Morales-Serna et al., 2010)
C_{60} and anthryl-PAMAM with 2 or 4 gluconamides	TOF (Sinapinic dithranol)	Optically pure fullerodendron formed by diastereoselective Diels-Alder reaction	(Takahashi et al., 2010)
Calixarene-based glycocluster oligonucleotide with 4 galactose residues	TOF	Click chemistry. Triazole-tethered glycoclusters with 3 arrangements. Affinities towards PA-IL and RCA 120 with DNA-based glycoarray.	(Moni et al., 2009)
Carbosilane with 3, 4 or 6 sialyl-α-(2→3)-lactose residues	TOF	For anti-influenza properties	(Oka et al., 2009)
Carbosilane with 3, 4, 6 or 12 Neu5Ac residues	TOF, FAB, ESI	Influenza neuraminidase inhibitors. Dendrimers uniformly functionalized with thioglycoside-type sialic acid moieties resistant to neuraminidases	(Sakamoto et al., 2009a)
Carbosilane with 8 or 16 mannose residues	TOF (dithranol)	Hydrosilylation of allyl tetra-Ac-Man with carbosilane dendrimers containing monohydrosilane end groups and the subsequent deacetylation	(Ortega et al., 2010)
Carbosilane with 4 sialyl-*N*-acetyllactosamine groups	TOF	Combined chemical and enzymatic synthesis	(Matsuoka et al., 2010)
Cyclic α-(1→6)-octaglucoside with from 2-7 mannose residues	TOF	Oxidation of *vic*-diols, reductive amination with 2-aminoethyl-mannoside	(Yang et al., 2010d)
β-Cyclodextrin with 27 mannose or glucose residues	TOF (DHB)	Heteroglycoclusters. 7 Antennae each with two mannose and one glucose. For lectin binding	(Gómez-García et al., 2010)
β-Cyclodextrin with dextran	TOF (CHCA)	Synthesis by click chemistry using Huisgen reaction	(Nielsen et al., 2010b)
Cyclopeptide with 4 mannose residues	TOF	Synthesis by click chemistry and molecular recognition study by surface plasmon resonance	(Chen et al., 2009c)
Dihydroxy-benzamide based with 2-8 mannose, galactose, lactose, glucose or GlcNAc groups	TOF (CHCA)	Octa-dendrimers. For screening of lectins for multivalency effects. Click chemistry	(Pera et al., 2010b)
Diphenyldisulfide with 4 glucose residues and others without sugars	TOF, GC/MS	Use as catalyst to convert allyl alcohols into carbonyl compounds	(Tsuboi et al., 2009)
Cysteine with 3 or 4 (from di-cysteine) mannose residues	TOF	As inhibitors of type 1 fimbriae mediated bacterial adhesion	(Schierholt et al., 2010)
Ethylene glycols with 2, 3 or 4 galactose,lactose, maltose or LacNAc groups	TOF (THAP)	Click chemistry. For improved avidity and selectivity in blocking human lectin/plant toxin binding to glycoproteins and cells	(André et al., 2010)

(*Continued*)

TABLE 31. (*Continued*)

Ferrocene with one or two glucose, mannose or lactose residues	TOF/TOF	As electrochemical probes for molecular recognition studies	(Casas-Solvas et al., 2009b)
Polyglycerol substituted phenylboronic acid	TOF	Dendrimer formed adducts with, Fru, D-(+)-Gal, D-(+)-Glc, D-(+)-Man, and Me-α-D- Man, by removal of four H_2O	(Hashidzume & Zimmerman, 2009)
Fullerene. Sugar balls with 12 iminoglucose residues	TOF	Synthesis by click chemistry. Glucosidase inhibition shown with resulting iminosugar balls	(Compain et al., 2010)
Fullerene. Sugar balls with 12 glucose or galactose residues	TOF, ESI, FAB	12 residues on 6 arms, Synthesis by click chemistry	(Nierengarten et al., 2010)
Gd-diethylenetri-aminepentaacetic acid with 2 glucose residues	TOF	Synthesis, *in vitro* and *in vivo* studies of Gd-DTPA-XDA-D1-Glc(OH) complex as a new potential MRI contrast agent	(Ozaki et al., 2010a)
Hydroxy benzenes and naphthalenes with 2, 4 or 8 mannose residues	TOF	Synthesis by click chemistry	(Rajakumar et al., 2009)
L-Lysine plus Gd chelates and 4 galactose residues	TOF/TOF	As liver imaging probes	(Luo et al., 2009)
MUC1 Peptide with 4 GalNAc, T antigen or sialyl-T_N antigens	MALDI	Fmoc solid-phase synthesis - as anti-cancer vaccine	(Chun & Payne, 2009)
PAMAM. Two to five generations with 16, 29, 55 and 95 mannose residues	TOF	For inhibition binding studies of glycodendrimer/lectin interactions using surface plasmon resonance	(Schlick & Cloninger, 2010)
PAMAM-NH_2 with 16 digoxin and proscillaridin A groups	TOF (DHB, CHCA)	16-Glycoside units. Synthesis and toxicity in breast cancer cells. Mass by MALDI = 15,672 Da	(Winnicka et al., 2010)
PAMAM (G4) with up to 47 lactose or GM3 glycans	TOF	Investigation of lactose·GM3 carbohydrate-carbohydrate interaction	(Seah et al., 2009)
PAMAM. 5^{th} generation with up to 64 maltose or maltotriose residues	L-TOF (CHCA)	UV/Vis and EPR study of metal ion complexation. Masses to 35 kDa	(Appelhans et al., 2010)
Pentaerythritol with 1-3 mannose or glucose residues	TOF (DHB)	For lectin binding	(Gómez-García, et al., 2010)
Pentaerythritol, glucose, galactose or trehalose with 4 or 8 α-Man, α-Glc, β-Glc residues	TOF (DHB)	Synthesis by click-based method. Binding affinities toward concanavalin A	(Ortega-Muñoz et al., 2009)
Peptide with 4 sialyl T_N glycodeca-peptide from MUC1	TOF (DHB, CHCA)	Tetramer of glycodecapeptide from MUC1 with sialyl T_N antigen as vaccine candidate	(Keil et al., 2009)
Peptide/tris-OH- methyl-methylamine. 9 galactose or mannose residues attached to β-CD containing doxorubicin	TOF	For uptake studies in the human hepatocellular carcinoma cell line HepG2	(Bernardes et al., 2010)
Peptide/tris-OH- Me-methylamine/ $[Ru(bipy)_3]^{2+}$ with 18 galactose or mannose residues	MALDI	To study lectin interactions by monitoring change in fluorescence quantum yield of Ru(II).	(Kikkeri et al., 2010a)
Phloroglucinol, triazyne, tetrachlorosilane, pentaerythritol, *myo*-inositol with 2, 3, 4 or 6 *C*-linked sialic acids	TOF	Synthesis by Huisgen cycloaddition of azide and alkyne (click chemistry). To explore sialic acid binding to cell surfaces	(Papin et al., 2009)
Phthalocyanine with 4 α-Gal*p* residues	TOF	Potential application as photosensitizers in photodynamic therapy	(Soares et al., 2009)
Pentaerythritol, methyl α-D-glucopyranoside, D-glucose, and D-mannitol with 4, 5 or 6 mannose	TOF (DHB)	Synthesis by click chemistry, Measurement of binding affinities	(Perez-Balderas et al., 2009)

TABLE 31. (*Continued*)

Polyester dendron with 4 trimannose residue	MALDI	Inhibition of DC-SIGN-mediated HIV infection by a linear trimannoside mimic in a tetravalent presentation	(Sattin et al., 2010)
Poly-glycerol with 8 mannose residues	TOF	MALDI poor because of high MW (up to 493 kDa)	(Kizhakkedathu et al., 2010)
Poly-lysine with 16 biantennary *N*-glycans	TOF	Synthesis by click chemistry. Effect of sialic acid linkage on *in vivo* dynamics. Mass around 40 kDa	(Tanaka et al., 2010b)
Poly-lysine on tris-(2-ethyl-amino)amine with 3 aulfated cellobiose groups	TOF (sDHB)	Synthesized by sulfation of polylysine-dendritic cellobiose (prepared from cellobiose and polylysine dendrimer generation 3)	(Han et al., 2010b)
Porphyrin with 8 lactose glycans	TOF	Synthesis by Huisgen click cycloaddition of azide and alkyne	(Okada et al., 2009b)
Porphyrin with galactose or lactose	MALDI	Synthesis by click chemistry. Activity on carcinogenic HEp2 cells	(Hao et al., 2009)
Poly(propyl-enimine) with 64 glycans from immune cell GSLs	L-TOF (IAA)	Inhibit infection by primary isolates of HIV-1. Masses up to 36 kDa	(Borges et al., 2010)
RAFT scaffold $(K\text{-}K\text{-}K\text{-}P\text{-}G)_2$ with 2, 4 or 6 LELTE glycopeptide containing GalNAc	FT-MS (CHCA, DHB)	Activators of natural killer lymphocytes	(Renaudet et al., 2010)
Ruthenium(II) bipyridine with 6 or 18 mannose or galactose residues	TOF	As probes to study lectin-carbohydrate interactions and to measure mono and oligo-saccharide concentrations electrochemically	(Kikkeri et al., 2010b)
Ruthenium porphyrins with 4 glucose residues	TOF	Water-soluble catalyst for carbenoid transfer reactions	(Ho et al., 2010)
Tetrabenzo-porphyrins with 4 glucose residues	TOF	To improve targeting of cancer cells	(Ménard et al., 2009)
Tetraphenyl-ethylene with 4 lactose or sialyl-lactose residues	TOF/TOF	Synthesis by click chemistry. As fluorescent probes for detection of influenza virus	(Kato et al., 2010b)
Tetraphenyl-ethylene with 4 or 8 mannose residues	TOF (DHB)	For fluorescence turn-on sensing of lectins based on aggregation-induced emission	(Sanji et al., 2010)
Dihydroxybenzamide base with 4 galabiose residues	TOF (CHCA)	For isolation of pathogenic *Streptococcus suis* bacteria	(Pera et al., 2010a)
1,3,5-Tris-(2-propynyloxy)-benzene with 3 β-cyclodextrin rings	TOF (DHB)	Synthesis by microwave-assisted click chemistry as fluorescent tripod detection system for pesticides	(Mallard-Favier et al., 2009)
Trimesic acid and others with 2, 3 or 4 phosphocholine residue related to glycol-sphingolipid from earthworm *Pheretima hilgendorfi*	TOF	For enhanced immune responses when compared to their monovalent counterparts	(Hada et al., 2009)
Various amino-alkyl with 2, 3 or 4 lactose residues	TOF (CHCA)	Synthesis from carbamate-linked lactose	(André et al., 2009)
Zinc(II) phthalocyanines with 8 Glc, Gal or cellobiose residues	TOF (DHB)	Chemical synthesis as photosensitizer in photodynamic therapy	(Iqbal et al., 2009a)
Zinc(II) phthalocyanines with 8 Glc, Gal, cellobiose or maltose residues	TOF (DHB, CHCA)	Eight residues. For photodynamic therapy	(Iqbal et al., 2010)
Zinc(II) naphthalocyanines with 4 glucose residues	TOF	As photosensitizer in photodynamic therapy	(Iqbal et al., 2009b)
Zinc(II) naphthalocyanine with 8 glucose or galactose residues	TOF, ESI	Ex post glycoconjugation	(Berthold et al., 2010)

[1]Format (not all items present): MALDI method (matrix). "MALDI" used when instrument not specified.

TABLE 32. Use of MALDI MS to Study Carbohydrate–Protein Conjugates

Sugar	Protein	Technique	Notes	Reference
Acid-detoxified lipopolysaccharide of *Vibrio cholerae* O1, serotype Inaba	BSA	TOF (DHB)	Free amino group on LPS used for site-specific conjugation. Towards bivalent immunogens	(Grandjean et al., 2009)
4-Amino-4-deoxy-L-arabinose (Ara4N)	maleimide-activated BSA	TOF (sinapinic)	Potent immunogen	(Müller et al., 2010a)
N-Acyl-modified sialylated glycans	HSA	TOF	Squaric acid chemistry. As inhibitors of adenoviruses causing epidemic kerato-conjunctivitis	(Johansson et al., 2009)
Biantennary *N*-glycan in transferrin	Transferrin	TOF	Toxic towards prostate cancer cells; induction of apoptosis	(Nakase et al., 2009)
3,6-Branched oligomannoside fragments from *Candida albicans*	BSA	TOF	Coupling to BSA by squarate method.	(Karelin et al., 2010)
Capsule polysaccharide from *Campylobacter jejuni*	CRM_{197}	L-TOF (sinapinic)	To prepare conjugate vaccine against diarrheal disease	(Monteiro et al., 2009)
Chitin oligosaccharides	BSA	TOF (CHCA)	Prepared with Maillard reaction	(Ledesma-Osuna et al., 2010)
Chitosan	DC101 antibody or IgG	TOF	For molecular imaging of VEGF receptors overexpressed in ischemic microvasculature	(Lee et al., 2010a)
Chlamydophila psittaci-specific branched Kdo trisaccharide epitope	BSA	TOF (DHB)	For the induction of *Chlamydophila psittaci*-specific monoclonal antibodies	(Kosma et al., 2010)
O-(3,6-di-*O*-methyl-β-D-Glc*p*)-(1→4)-*O*-2,3-di-*O*-methyl-α-L-Rha*p* from *Mycobacterium leprae*	BSA/HSA	TOF	For commercialization of diagnostic kits and high-throughput detection of leprosy	(Zhang et al., 2010b)
Gal, 2-keto-Gal + fluorescent probe	Single-chain antibody	TOF	Method for drug targeting using antibodies	(Ramakrishnan et al., 2009)
Galactose	BSA	TOF	New photoinduced thiol-ene coupling	(Dondoni et al., 2009)
Galactose	HSA	TOF	Two step synthesis of Gal_{28} as optical imaging agent for peritoneal carcinomatosis	(Regino et al., 2010)
Ginsenoside Rg3	BSA	TOF (sinapinic)	Generation and characterization of monoclonal antibody to ginsenoside Rg3	(Joo et al., 2009)
α-Glc, α-Man, β-Gal, α-Fuc, β-Fuc	HSA	TOF	Biodistribution and excretion measured with *in vivo* near-infrared fluorescence imaging	(McCann et al., 2010)
Helminth antigen (GalNAcβ1-4(Fucα1-3)GlcNAcβ-R)	BSA	L-TOF/TOF	Chemoenzymatic synthesis. To study role on antigen in immune system interaction	(Tefsen et al., 2009)
Heparin tetra-saccharide	Complement factor H	TOF (sinapinic, CHCA)	Study of interaction between protein and tetrasaccharide by cross-linking	(Blaum et al., 2010)

TABLE 32. (*Continued*)

Heptasaccharide fragment of the cell wall mannan from *Candida guilliermondii*	BSA	TOF/TOF (DHB)	Synthesis by convergent approach - glycosylation of a tetrasaccharide acceptor with trisaccharide donor and squarate conjugation to BSA	(Karelin et al., 2009)
Hexasaccharide fragment of O-PS of *Vibrio cholerae* O:1, serotype Inaba	Tetanus toxin H_C fragment	SELDI-TOF	Squaric acid chemistry. Preparation of multimeric bivalent immunogens	(Bongat et al., 2010)
Lactose	BSA	TOF	Direct amidation of free carbohydrates for direct coupling	(Cho et al., 2009a)
D-Lactose	BSA	L-TOF (CHCA)	Synthesis under various conditions. Study of lectin binding	(Ledesma-Osuna et al., 2009)
Lewis b pentasaccharide	HSA	TOF (THAP)	To study carbohydrate recognition processes by *Helicobacter pylori*	(Fournière et al., 2010)
LPS from *Salmonella enterica* sv. Minnesota	HRP	TOF	Use of surfactant-assisted LPS conjugation employing a cyanopyridinium agent	(Pallarola & Battaglini, 2009)
Mannose	Recombinant, HSA, BSA	TOF	Genetically engineered Man-HSA as carrier for liver-selective therapeutics	(Hirata et al., 2010)
α-Mannosides (bi- and penta-)	BSA	TOF	Immunogenicity and induction of candidacidal activity	(Paulovičová et al., 2010)
Methyl glyoxal (advanced glycation end product, (AGE))	HSA	TOF/TOF	Effect of AGE-ligands on the regulation of AGE receptor isoforms and the consequences on red blood cell adhesion.	(Grossin et al., 2010)
N-glycans	HSA and lymphocytes	TOF, ESI	Combined 6π-azaelectrocyclization/ Staudinger method	(Tanaka et al., 2010a)
O-Deacylated LPS from *Neisseria meningitidis*	Diphtheria toxin mutant CRM197	L-TOF (sinapinic)	Chemical strategies to prepare glycoconjugates with good carbohydrate loading. For immunology: (Cox et al., 2010b)	(Cox et al., 2010a)
O-specific core fragments from *Shigella flexneri* 2a and 6, and *Shigella dysenteriae* type 1	BSA	L-TOF (sinapinic)	Preparation and immunological studies	(Kubler-Kielb et al., 2010)
Oligomannosides	Icosahedral capsids of bacteriophage Qβ, cowpea mosaic virus	MALDI	To investigate criteria for design of oligomannose immunogens for HIV	(Astronomo et al., 2010)
6-PEt*N*-α-D-Gal*p*NAc-(1→6)-β-D-Gal*p*-(1→4)-β-D-Glc*p*NAc-(1→3)-β-D-Gal*p*-(1→4)-β-D-Glc*p*	HSA	TOF	Synthesis of sugar (from *Haemophilus influenzae*) and conjugation to HSA	(Sundgren et al., 2010)
Polysialic acid	Insulin	MALDI	Shown to increase insulin lifetime *in vivo*	(Bezuglov et al., 2009)
Serogroup 6 pneumococcal oligosaccharides	BSA	SELDI-TOF, FAB	Synthetic carbohydrate conjugates express epitopes found in native capsular polysaccharides	(Parameswar et al., 2009)

(*Continued*)

TABLE 32. (*Continued*)

Shigella sonnei O-specific core oligosaccharide	BSA, diphtheria toxin	L-TOF (sinapinic)	Synthesis, characterization, and immunogenicity in mice	(Robbins et al., 2009)
Shigella sonnei LPS	BSA, Diphtheria toxin	TOF	Synthesis, characterization, and immunogenicity.	(Kubler-Kielb et al., 2009)
Terminal monosaccharide antigen of the O-PS of *Vibrio cholerae* O1, serotype Ogawa	BSA	TOF/TOF (CHCA)	Synthesised by squaric acid chemistry. Glycation sites determined by MALDI tandem MS (see text)	(Jahouh, et al., 2010)
Tn antigen	HSA	MALDI	To study effects of hapten density on induced antibody repertoire	(Li et al., 2010c)
Tumor-associated MUC1 glycopeptides	Lipopeptide ligand of toll-like receptor 2	TOF	Synthesis of synthetic vaccines	(Kaiser et al., 2010)
Tumor-associated sialyl-T_N-MUC1 glycopeptides	BSA, tetanus toxoid	TOF	Synthesis of synthetic vaccines. Strong and selective immune response	(Kaiser et al., 2009)
Tumor-associated sialyl-T_N-MUC1 glycopeptides	BSA, tetanus toxoid	TOF (DHB)	Synthesis of synthetic vaccines. Strong and selective immune response	(Hoffmann-Röder et al., 2010)
Various	BSA	TOF/TOF	Use of *p*-nitrophenyl anthranilate as a heterobifunctional linker	(Luyai et al., 2009)
Various	BSA	TOF	To construct microarrays for screening antibodies	(Oyelaran et al., 2009)
Various	BSA	TOF (sinapinic)	To study multivalent binding to human α-defensin (HD5)	(Lehrer et al., 2009)

[1]Format: MALDI method (matrix).

CHCA	α-cyano-4-hydroxycinnamic acid
CHO	Chinese hamster ovary
CID	collision-induced dissociation (decomposition)
CMBT	5-chloro-2-mercaptobenzothiazole
ConA	concanavalin A
Con A	concanavalin A (lectin)
CoV	coronavirus
Cys	cysteine
Da	Dalton
DC-SIGN	dendritic cell-specific ICAM3-grabbing nonintegrin
DCTB	2-[4-*tert*-butylphenyl-2-methylprop-2-enylidene]-malonitrile
DEA	dissociative electron attachment
Dha	3-deoxy-D-lyxo-2-heptulosonic acid
DHAP	dihydroxyacetophenone (2,6-unless stated otherwise)
DHB	dihydroxybenzoic acid
DMA	*N*,*N*-dimethylaniline
DMAN	1,8-*bis*(dimethylamino)naphthalene
DMB	1,2-diamino-4,5-methylenedioxybenzene
DMSO	dimethylsulfoxide
DMT-MM	4-(4,6-dimethoxy-1,2,3-triazil-2-yl)-4-methylmorpholinium chloride
DNA	deoxyribonucleic acid
Dol	dolichol
DOPA	L-3,4-dihydroxyphenylalanine
DP	degree of polymerization
DSA	*Datura stramonium* agglutinin (lectin)
DTT	dithiothreitol
ECM	extra-cellular matrix
EDC	1-ethyl-3-(3-imethylaminopropyl) carbodiimide hydrochloride
EDI	electrospray droplet impact
EDTA	ethylenediaminetetraacetic acid
CEACAM1	carcinoembryonic antigen-related cell adhesion molecule 1
Endo-F (H, M)	endoglycosidase-F (H, M)
EPO	erythropoeitin
EPR	electron paramagnetic resonance
EPS	extracellular polysaccharide
ER	endoplasmic reticulum
ESI	electrospray ionization
ETD	electron transfer dissociatiom
EtN	ethanolamine
f (as in Gal*f*)	furanose form of sugar ring
FAB	fast atom bombardment
FACE	fluorophore-assisted carbohydrate electrophoresis

FAIMS	field asymmetric waveform ion mobility spectrometry
Fc	fragment (crystallisable) region of IgG
Fmoc	9-fluorenylmethoxycarbonyl
Fru	fructose
F-SPE	fluorous solid phase extraction
FT	Fourier transform
Fuc	fucose
G0 (G1, G2)	biantennary glycans with 0, (1 or 2) galactose residues
G3CA	coumaric 1,1,3,3,-tetra-methylguanidine
GABA	gamma-aminobutyric acid
GAGS	glycosaminoglycans
Gal	galactose
GalA	galacturonic acid
GalN	galactosamine
GalNAc	*N*-acetylgalactosamine
G3CA	coumaric 1,1,3,3,-tetra-methylguanidine (liquid matrix)
GaPcs	gallium-phthalocyanines
GC/MS	gas chromatography/mass spectrometry
GD1a	ganglioside αNeu5Ac-(2 → 3)-β-D-Gal*p*-(1 → 3)-β-D-GalNAc-(1 → 4)-[αNeu5Ac(2-3)]-β-D-Gal*p*-(1 → 4)-β-D-Glc*p*-(1 → 1)-Cer
Glc	glucose
GLC	gas–liquid chromatography
GlcA	glucuronic acid
GlcN	glucosamine
GlcNAc	*N*-acetylglucosamine
Gln	glutamine
Glu	glutamic acid
Gly	glycine
GM1	ganglioside (β-D-Gal*p*-(1 → 3)-β-D-GalNAc[αNeu5Ac(2 → 3)]-β-D-Gal*p*-(1 → 4)-β-D-Glc*p*(1 → 1)Cer)
GM3	ganglioside (αNeu5Ac-(2 → 3)-β-D-Gal*p*-(1 → 4)-β-D-Glc*p*-(1 → 1)Cer)
GMDB	glycan mass spectral database
GnT	GlcNAc transferase
GPI	glycosyl-phosphatidylinositol
GRIL	glycan reductive isotope labeling
GSL	glycosphingolipid
GT	*galacto*-trehalose
GX	glucuronoxylan
HABA	2-(4′hydroxyphenyl)azobenzoic acid
HALSs	hindered amine light stabilizers
HARE	hyaluronic acid receptor for endocytosis
HD5	human α-defensin
HEK	human embryonic kidney
Hep	heptose
Hex	hexose
HexA	hexuronic acid
HexNAc	*N*-acetylhexosamine
HF5	hollow fiber flow field-flow fractionation
HFBA	heptafluorobutyric acid
HFMP	hydrazine functionalized carboxyl and epoxysilanized magnetic particles
hFSH	human follicle-stimulating hormone
HILIC	hydrophilic interaction chromatography
HIQ	hydroxyisoquinoline
HIV	human immunodefficiency virus
HLG2	ganglioside (Neu5Gc-α-(2 → 4)-Neu5Ac-α-(2 → 6)-Glc*p*-(1 → 1)Cer)
HM	high mass
HNK	human natural killer
HPA	hydroxypicolinic acid
HPAEC	high-performance anion exchange chromatography
HPLC	high performance liquid chromatography
HRP	horseradish peroxidase
HS	heparan sulfate
HSA	human serum albumin
ICAM	intercellular adhesion molecule
ICR	ion cyclotron resonance
IdoA	iduronic acid
IgA (G or M)	immunoglobulin A (G or M)
IGOT	isotope-coded glycosylation site-specific tagging
InPcs	indium-phthalocyanines
IR	infrared
IRMPD	infrared multiphoton dissociation
ISD	in-source decay
IT	ion trap
ITO	indium-tin oxide
IUPAC	International Union of Pure and Applied Chemistry
KDEL	peptide sequence (Lys-Asp-Glu-Leu)
Kdo	3-deoxy-D-*manno*-oct-2-ulosonic acid
KEGG	Kyoto encyclopedia of genes and genomes
Ko	D-*glycero*-D-*talo*-oct-2-ulosonic acid
L-	linear (as in linear-TOF)
Lac	lactose (Gal-β-(1 → 4)-Glc)
LAC	ligand affinity capture
LacdiNAc	GalNAc-β-(1 → 4)-GlcNAc
LacNAc	*N*-acetyl-lactose (Gal-β-(1 → 4)-GlcNAc)
LAM	lipoarabinomannan
LC	liquid chromatography
LDMS	laser desorption mass spectrometry
LIF	laser-induced fluorescence
LNDFH	lacto-di-fucohexaose
LNFP	lacto-*N*-fucopentaose
LOD	limit of detection
LOS	lipooligosaccharide
LPS	lipopolysaccharides
LTQ	linear trap quadrupole
LTA	lipoteichoic acid
LTQ	linear quadrupole ion trap mass spectrometer
Lys	lysine
MAb (MAB)	monoclonal antibody
MALDI	matrix-assisted laser desorption/ionization mass spectrometry
MalZ	maltodextrin glucosidase
Man	mannose
ManNAc	*N*-acetylmannosamine
MDBK	Madin–Darby bovine kidney cells
MEL	mannosyl-erythritol lipid
mf-MELDI	matrix-free material-enhanced laser desorption/ionization mass spectrometry
MHC	major histocompatibility complex
MOSF	*Macroporous silica* foam

MPc	metal-phthalocyanines
MS	mass spectrometry
MSI	mass spectrometric imaging
MS^n	MS fragmentation n times
MTT	3-methyl-1-*p*-tolyltriazene
MUC	mucin
MW	molecular weight
MurNAc	*N*-acetyl muramic acid
m/*z*	mass to charge ratio
4-NA	4-nitroaniline
NAcLac	*N*-acetyllactosamine
NAc-NAc	*N*-acetyl-lactosamine
NAIM	naphthimidazole
NALDI	nano-assisted laser desorption-ionization
nano-PALDI	nanoparticle-assisted laser desorption/ ionization
NBD	7-nitro-2,1,3-benzoxadiazole
Nd:YAG	neodymium-doped yttrium aluminium garnet (laser)
Neu5Ac	*N*-acetylneuraminic (sialic) acid
Neu5Gc	*N*-glycoylneuraminic acid
NIMS	nanostructure-initiator mass spectrometry
NIS	*N*-iodosuccinimide
NMR	nuclear magnetic resonance
NOD	nodulation (as in nodulation factor)
NP	normal phase
OCN	oscillating capillary nebulizer
OEG	oligo (ethylene glycol)
ORD	optical rotatory dispersion
OS	operating system
p (as in Gl*cp*)	pyranose form of sugar ring
PAD	pulsed amperometric detection
PAEA	2-(2-pyridylamino)ethylamine
PAF	platelet-activating factor
PAGE	polyacrylamide gel electrophoresis
PAH	polycyclic aromatic hydrocarbon
PAMAM	poly(amidoamine)
PBS	phosphate buffered saline
PCR	polymerase chain reaction
PEG	polyethylene glycol
PET	positron emission tomography
PEt*N*	phosphoethanolamine
PGM	porcine gastric mucin
Phe	phenylalanine
PI	phosphatidylinositol
PIM	phosphatidyl-*myo*-inositol mannosides
PKB	proteine kinase B
PMG	pyrenemethylguanidine
PNG	Portable Network Graphics
PNGase	protein-*N*-glycosidase
PNIPAM	poly(*N*-*iso*propylacrylamide)
Ppg	polyprenylphospho-GalNAc
PPM	polyprenolphoshomannose
PS	polysaccharide
PSA	porcine serum albumin
PSD	post-source decay
Pse	5,7-diamino-3,5,7,9-tetradeoxy-L-*glycero*-L-*manno*-non-2-ulosonic acid (pseudaminic acid)
PSGL	P-selectin glycoprotein ligand
psi	Pounds per square inch
Psi	psicose
PVDF	polyvinylidine difluoride
PyAOP	(7-azabenzotriazol-1-yloxy) *tris*-pyrrolidinophosphoniumexafluoro-phosphate
Q	quadrupole
QIT	quadrupole ion trap
R-	reflectron (as in R-TOF)
RA	rheumatoid arthritis
RAFT	reversible addition-fragmentation chain transfer
RGM	rat gastric mucin
Rha	rhamnose (6-deoxymannose)
RNA	ribonucleic acid
RNase	ribonuclease
RP	reversed phase
SALDI	surface-assisted laser desorption/ ionization
SAM	self-assembled monolayer
SARS	severe acute respiratory syndrome
s-DHB	super-DHB (DHB + 2-OH,5-OMe-benzoic acid)
SD	standard deviation
SDS	sodium dodecyl sulfate
SEC	size-exclusion chromatography
SEKDEL	peptide sequence (Ser–Glu–Lys–Asp–Glu–Leu)
SELDI	surface-enhanced laser desorption/ ionization
SEM	secondary electron multiplier
Ser	serine
sIgA	secretory IgA
SIMS	secondary ion mass spectrometry
S/*N*	signal-to-noise ratio
SORI	sustained off resonance irradiation
SPR	surface plasmon resonance
SPE	solid-phase extraction
SrtA	sortase A
STL	succinoyl trehalose lipid
SynCAM	synaptic cell adhesion molecule
-T (as GlcNAc-T)	transferase
Tal	talose
TB	tuberculosis
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
TF	transferrin
TFA	trifluoroacetic acid
THAP	trihydroxyacetophenone (usually 2,4,6-isomer)
THP1	human acute monocytic leukemia cell line
Thr	threonine
TLC	thin-layer chromatography
TMG	*N*,*N*,*N*-trimethyl-D-glucosamine
TMPP	tris(2,4,6-trimethoxyphenyl)phosphonium derivative
TMS	trimethylsilyl
TMSOTf	trimethylsilyl triflate
TNF	tumor necrosis factor
TOF	time-of-flight
TOSIL	tandem ^{18}O stable isotope labeling
TPA	tissue plasminogen activator
TROC	2,2,2-trichlororthoxycarbonyl
Trp	tryptophan

TWIMS	traveling wave ion mobility spectrometry
Tyr	tyrosine
UDP	uridine diphosph(ate)(o)
UV	ultraviolet
VEGF	vascular endothelial growth factor
VPBA	4-vinylphenylboronic acid
vWF	von Willebrand factor
WGA	wheat germ agglutinin (lectin)
WT	wild type
X	xylose
X_nG_n	xyloglucans (e.g., XXXG)
XOS	xylooligosaccharides
Xxx	any amino acid
Xyl	xylose
XyG	xyloglucan
ZIC-HILIC	zwitterionic hydrophilic interaction liquid chromatography

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