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A Systematic Nomenclature for Carbohydrate Fragmentations in FAB-MS/MS Spectra of Glycoconjugates

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A summary of the ion types observed in the Fast Atom Bombardment Mass Spectrometry (FAB-MS) and collision induced decomposition (CID) MS/MS spectra of glycoconjugates (glycosphingolipids, glycopeptides, glycosides and carbohydrates) is presented. The variety of product ion types that arise by cleavages within the carbohydrate moieties has prompted us to introduce a systematic nomenclature to designate these ions. The proposed nomenclature has been developed primarily for FAB-MS, but can be used as well for other ionization techniques [field desorption (FD), direct chemical ionization (DCI), laser desorption/Fourier transform (LD/FT), etc.], and is applicable to spectra recorded in either the positive or negative ion mode during both MS and MS/MS experiments.

A_i, B_i and C_i labels are used to designate fragments containing a terminal (non-reducing end) sugar unit, whereas X_j, Y_j and Z_j represent ions still containing the aglycone (or the reducing sugar unit). Subscripts indicate the position relative to the termini analogous to the system used in peptides, and superscripts indicate cleavages within carbohydrate rings.

FAB-MS/MS spectra of a native glycosphingolipid and glycopeptide, and a permethylated ganglioside are shown as illustrations.

Fast atom bombardment mass spectrometry [1] is now a well-established method for the analysis of large and polar molecules. Its application to glycoconjugates has been

Abbreviations: FAB-MS, fast atom bombardment mass spectrometry; CID, collision induced decomposition; DCI, direct chemical ionisation; FD, field desorption; LD/FT, laser desorption/Fourier transform; EI, electron impact; G_{M1}-ganglioside, II^3NeuAc-GgOse$_4$Cer; Fuc-GM1, IV^2Fuc,II^3NeuAc-GgOse$_4$Cer; hex, hexose; hexNAc, *N*-acetylhexosamine.

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reviewed [2]. The recent commercial availability of high performance tandem mass spectrometers (MS/MS) has added a new dimension in the structure elucidation of biomolecules [3]. In this type of MS/MS experiment, the ion associated with the molecular weight ($[M+H]^+$, $[M-H]^-$) or a fragment ion is selected by the first of two double-focusing mass spectrometers (MS-1) at a resolution of one mass unit. These mass-selected precursor ions collide with an inert gas such as helium in a collision cell located in the field-free region between MS-1 and MS-2, and the decomposition products are transmitted to MS-2 (or in the absence of a collision gas, the products of unimolecular decomposition can be transmitted). Finally, the product ions are analyzed, also at unit resolution, in the second mass spectrometer (MS-2). A major advantage of this two-step process is that mixtures can be analyzed in a manner that yields structural information related solely to the ion selected by MS-1. This technique is particularly useful for the analysis of glycoconjugates, which are commonly heterogeneous samples. By this means, the structure of each individual component can be established directly from the mixture [4].

Investigation of glycoconjugates (glycolipids and glycopeptides) as well as glycosides (triterpene and steroid saponins) by FAB-MS and FAB-MS/MS has shown that the fragmentation patterns within the carbohydrate portion can be rather complex, especially for CID-MS/MS spectra [2, 4-8]. Various symbols have already been used to designate the fragments observed in the two sector FAB-MS spectra of these compounds [2, 9]. Additional fragmentation pathways now being recognized in CID-MS/MS spectra lead to product ions that cannot be accommodated with any of these systems. Some of these fragments also appear in carbohydrate mass spectra obtained by laser desorption/Fourier transform mass spectrometry (LD/FT-MS) [10]. The earlier system developed to delineate the extensive fragmentation observed in the electron impact (EI) mass spectra of monosaccharides and small oligosaccharides [11, 12] becomes unwieldy when applied to very large, branched structures, because it requires an additional letter for each sugar residue and does not have a designation for multiple branches.

We are thus prompted to introduce a systematic nomenclature for labelling the fragment-ions observed both in FAB-MS and FAB-MS/MS spectra. This proposed nomenclature has been devised by analogy to that in use for peptides [13, 14], although the structures of carbohydrates necessitate the use of somewhat more complex symbols. We use an extension of the system described here to designate fragmentation within the aglycone of glycosphingolipids [4]. When lower-case letters are used to designate peptide cleavages [15], the system proposed here serves to describe cleavages within the carbohydrate portion of glycopeptides. Because few spectra of this type have yet appeared in the literature, we present here a few examples to show typical spectra and how the nomenclature system can be applied to assign product ions.

Materials and Methods

Materials

G_{M1}-Ganglioside (GM1) and asialo-G_{M1}-ganglioside were obtained from Sigma Chemical Co., St. Louis, MO, USA. The glycopeptide originating from human serotransferrin [16] was obtained from BioCarb Chemicals, Lund, Sweden. G_{M1}-Ganglioside

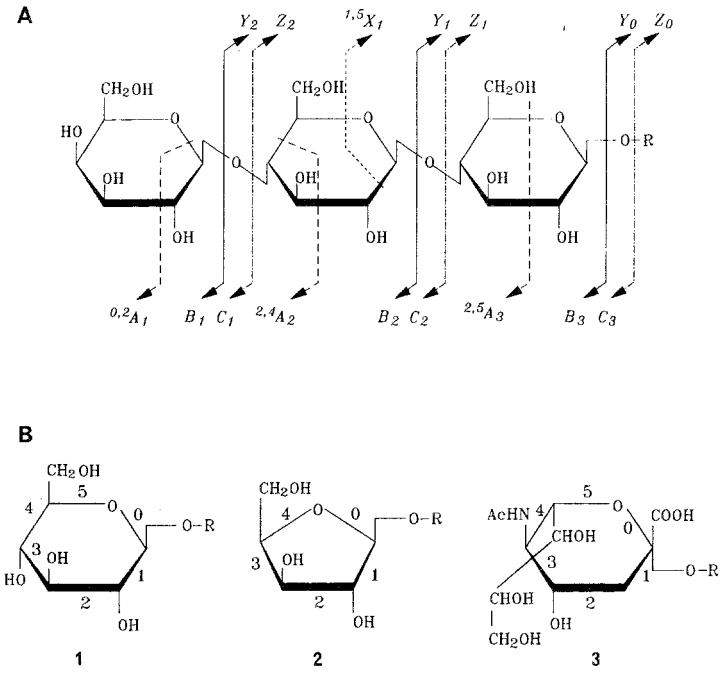

Figure 1. Types of carbohydrate fragmentation.

was permethylated by the method of Ciucanu and Kerek [17], as modified by Larson *et al.* [18]. Samples were dissolved in dimethylsulfoxide (glycosphingolipids and derivatives) or water (glycopeptides) at a concentration of 5 μg/μl and then mixed with an equal volume of glycerol/dithiothreitol/dithioerythritol, 4/3/1 by vol, for positive ion spectra or triethanolamine for negative ion spectra. About 0.3 μl of the resulting mixture were used for the analysis.

Fast Atom Bombardment Mass Spectrometry

FAB-MS was carried out on the first (MS-1) of the two mass spectrometers of a tandem high resolution mass spectrometer (JEOL HX110/HX110) at 10 kV accelerating voltage and 1:1500 resolution. $(CsI)_nCs^+$ and $(CsI)_nI^-$ cluster ions were used for calibration in the positive and negative ion modes, respectively. Single scans were acquired by scanning the magnet from m/z 200 to 2000 in about 2.0 min. The JEOL FAB gun was operated at 6kV to produce the neutral xenon beam.

Tandem Mass Spectrometry

FAB-MS/MS was carried out by using all four sectors of the JEOL HX110/HX110 spectrometer, an instrument of E_1B_1-E_2B_2 configuration. Collision-induced decomposition took place in the third field free region, thus both MS-1 (E_1B_1) and MS-2 (E_2B_2) were

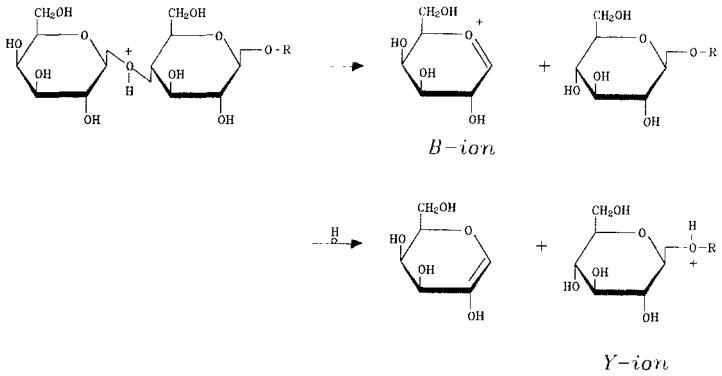

Figure 2. Genesis of B_i and Y_j ions in the positive ion mode.

operated as double focusing instruments. Helium was used as the collision gas at a pressure sufficient to reduce the precursor ion signal by 50-80%. The FAB-MS/MS spectra (linked scans of MS-2 at constant B/E ratio) were recorded during 2 min scans with 30 Hz filtering. Resolution of MS-2 was usually 1:1000. The MS-2 was calibrated with a micture of CsI, NaI, KI and LiCl in the positive ion mode and a solution of CsI in glycerol in the negative ion mode, and mass assignment accuracy was within 0.3 units of the calculated values [19]. FAB-MS/MS spectra shown are profile data of two or three accumulated scans.

Results and Discussion

Fragmentation of the Oligosaccharide

The simplest fragmentation of the carbohydrate moiety of glycoconjugates and glycosides occurring during FAB-MS and FAB-MS/MS results from the cleavage of the glycosidic bond and thus yields information regarding the sugar sequences. More complex processes involving the fragmentation of the sugar ring have been observed, particularly in CID-MS/MS spectra [3, 5]. Such ions, although more difficult to assign, still contain pertinent structural information. Since spectra recorded in both positive and negative ion modes have shown such fragmentation, we here suggest use of a common nomenclature.

As illustrated in Fig. 1A, when the charge is retained on the carbohydrate portion, fragments are designated as A_i, B_i and C_i, where i represents the number of the glycosidic bond cleaved, counted from the non-reducing end (the case of branched oligosaccharides will be discussed below). On the other hand, ions containing the aglycone (or the reducing sugar unit in the case of oligosaccharides) are labeled as X_j, Y_j and Z_j, where j is the number of the *interglycosidic* bond counted from the aglycone (or the reducing end for carbohydrates). The glycosidic bond linking to the aglycone is numbered 0.

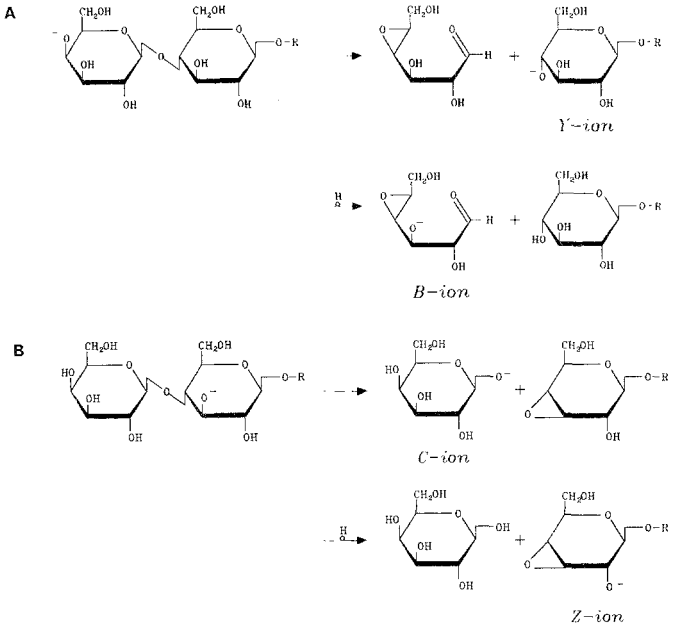

Figure 3. Negative ion geneses of A) B_i and Y_j, and B) C_i and Z_j.

Cleavage of the Glycosidic Bond

The more common fragmentations occurring in the spectra of glycoconjugates and glycosides involve cleavage of the glycosidic bond, with retention of the glycosidic oxygen atom by the species formed from the reducing end. Fragment ions generated by this cleavage are observed in both positive and negative ion spectra and are represented as B_i and Y_j.

In the positive ion mode, the fragments result from protonation of the glycosidic bond, which is subsequently broken to yield the B_i oxonium ion and a smaller glycoconjugate (Fig. 2). Alternatively, cleavage of the glycosidic bond could be accompanied by a proton transfer which would thus yield the complementary Y_j, with j = n-1 for a linear oligosaccharide constituted of n sugar units.

In the negative FAB ion mode, this type of fragmentation follows a more complex pathway, as formulated in Fig. 3A. On the basis of an experiment that led to $H/^2H$ exchange of the hydroxyl proton and an investigation of glycosides containing selectively derivatized hydroxyl groups, Prome *et al.* [20] have proposed that the deprotonated molecular ion (a proton having been abstracted from a hydroxyl group in position 4 or 6) undergoes epoxide formation accompanied by opening of the sugar ring and, finally, cleavage of the glycosidic bond to yield the Y_j-ion. A competitive H-transfer may occur to produce the B_i-ion.

Table 1. Summary and nomenclature for carbohydrate fragmentations occurring in FAB MS and FAB MS/MS spectra of glycoconjugates.

Fragment	Positive ion mode[a]	Negative ion mode
A_i	Seldom observed.	Various type of fragmentation involving H-transfer:[b] $A_i^- = [A_i \pm xH]^-$ e.g. m/z 119, $[^{0,2}A_1\text{-}H]^-$.
B_i	Simple cleavage of the protonated glycosidic bond: $B_i^+ = [B_i]^+$ e.g. m/z 163, B_1^+.	Deprotonation followed by an H-transfer: $B_i^- = [B_i\text{-}2H]^-$ e.g. m/z 161, B_1^-.
C_i	H-transfer (and protonation): $C_i^+ = [C_i+2H]^+$ e.g. m/z 181, C_1^+.	Deprotonation of the adjacent sugar ring, then simple cleavage: $C_i^- = [C_1]^-$ e.g. m/z 179, C_1^-.
X_j	Various types:[b] $X_j^+ = [X_j \pm xH]^+$ e.g. $[M+H-134]^+$, $[^{1,5}X_{n-1}+H]^+$	Various types:[b] $X_j^- = [X_j \pm xH]^-$ e.g. $[M\text{-}H-134]^-$, $[^{1,5}X_{n-1}\text{-}H]^-$.
Y_j	Cleavage of the protonated glycosidic bond followed by an H-transfer: $Y_j^+ = [Y_j+2H]^+$ e.g. $[M+H-162]^+$, Y_{n-1}^+.	Deprotonation inducing a simple cleavage: $Y_j^- = [Y_j]^-$ e.g. $[M\text{-}H-162]^-$, Y_{n-1}^-.
Z_j	Formally simple cleavage, but more likely a two-step process involving a loss of water from the corresponding Y_j ion: $Z_j^+ = [Z_j]^+$ or $Z_j^+ = (Y_j^+\text{-}H_2O)$ e.g. $[M+H-180]^+$, Z_{n-1}^+.	H-transfer following the deprotonation: $Z_j^- = [Z_j\text{-}2H]^-$ e.g. $[M\text{-}H-180]^-$, Z_{n-1}^-.

[a] The examples shown in this table correspond to fragmentation of the terminal hexose unit of a linear oligosaccharide containing n sugar units.
[b] The H-transfers should be specified in each case: x = 0,1,2,3.

An alternative process frequently observed in the negative ion mode is fragmentation of the glycosidic bond with retention of the glycosidic oxygen, as formulated in Fig. 3B. In this case, deprotonation is assumed to occur on a hydroxyl group adjacent to the linked sugar moiety. The resulting oxyanion can then undergo epoxide formation and expel the substituent, to yield a C_i-ion. Here again, this process may be accompanied by an H-transfer, to produce a Z-ion, and occurs readily even without collision [1].

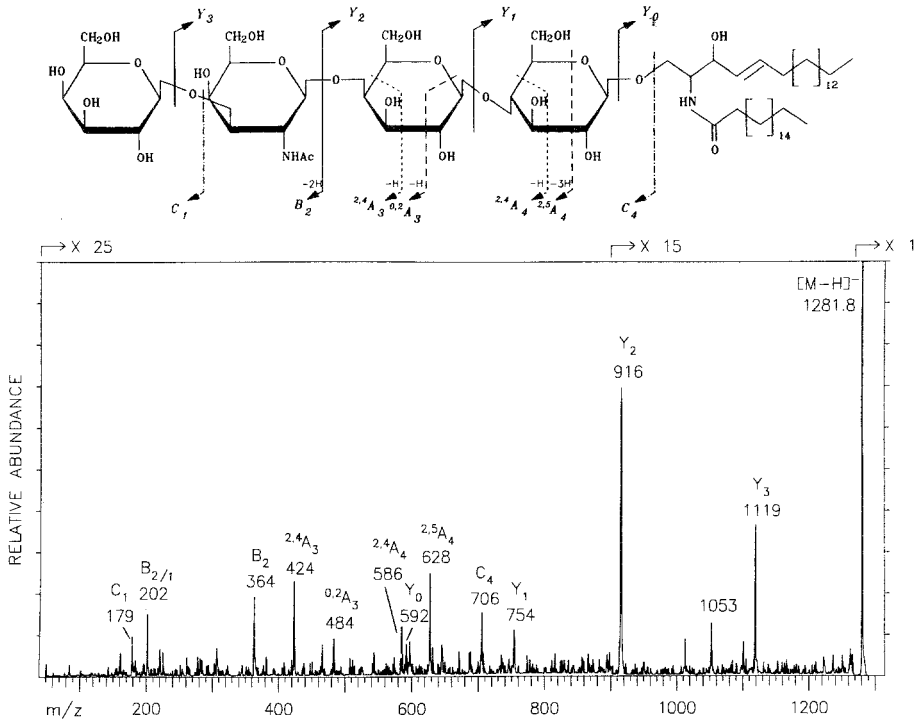

Figure 4. Negative FAB-CID-MS/MS spectrum of asialo-G_{M1}-ganglioside and assignment of product ions; precursor $[M-H]^-$, m/z 1281.8.

Sugar Ring Fragmentation

More complex pathways involve cleavages of carbon-carbon bond(s) of the sugar ring and have been observed in the FAB-CID-MS/MS spectra of glycoconjugates [4, 7, 8] and in LD/FT-MS spectra [10]. The product ions are designated with A_i and X_j labels. Since several such fragmentations are possible, a systematic representation requires additional symbols. We suggest the use of two superscripts k and l (i.e. $^{k,l}A_i$ and $^{k,l}X_j$) to indicate the sugar ring bonds that have been broken. The numbering of the ring bonds is specified in Fig. 1B for the sugar moieties commonly encountered. The use of a superscript to the left of the symbol provides a designation that may be easily handled by editing and typesetting programs and should avoid confusion of these symbols with those of the Kochetkov-Chizhov system [11].

Table 1 summarizes the various types of fragmentation and the corresponding H-transfers involved, for positive and negative ions. Proton transfers accompanying B_i, C_i, Y_j and Z_j fragments are predictable and do not need to be specified in each case. For A_i and X_j, the situation is more complex, and the proton transfers need to be specified (e.g. $(^{2,4}A_2\text{-H})^-$, $(^{0,2}A_1\text{-H})^-$ observed at m/z 221 and 119 respectively, in the collision spectra

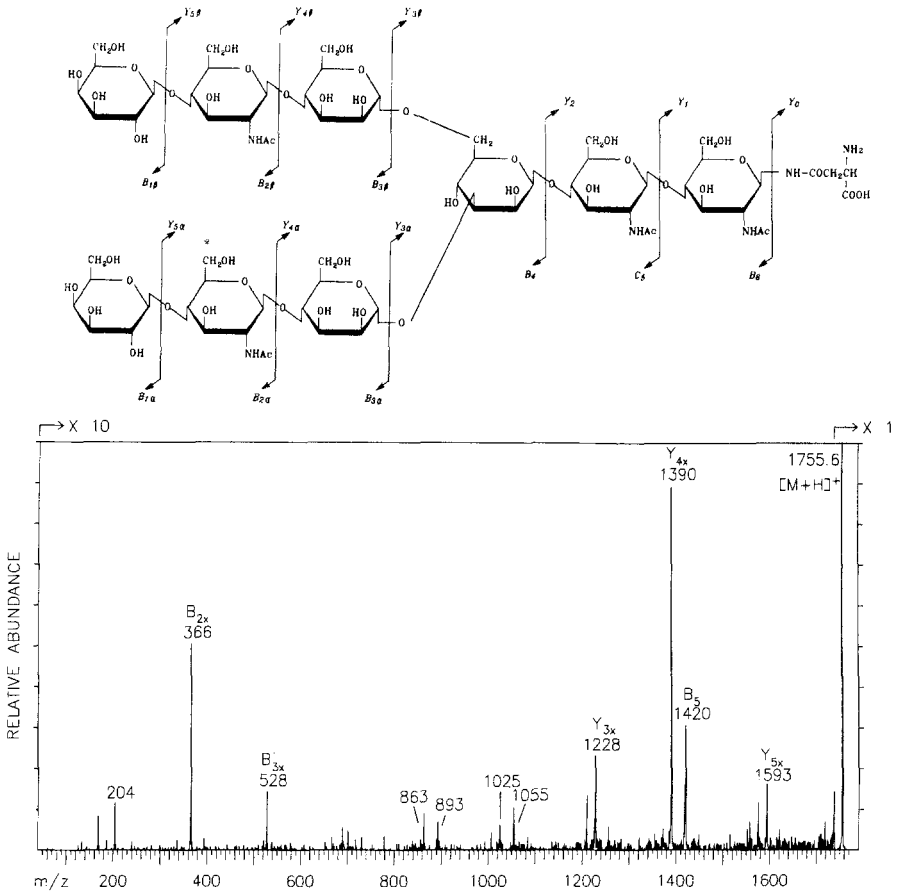

Figure 5. Positive FAB-CID-MS/MS spectrum of an asialo bi-antennary glycoasparagine from human serotransferrin and assignment of product ions; precursor $[M+H]^+$, m/z 1755.6. Fragments that can originate from either antenna α or β bear the subscript x on the plotted spectrum. Ions for which m/z values but not symbols appear are second generation fragments whose assignments are discussed in the text.

of lactosides [4]). A_i-Ions are seldom observed in positive ion spectra. X_j-Ions occur frequently in positive ion spectra but only rarely in negative ion spectra (unpublished results from this laboratory).

As an illustration, Fig. 4 shows the negative ion FAB-MS/MS collision spectrum and the assignment of the product ions for the glycosphingolipid asialo-GM1 (precursor: $[M-H]^-$ ion at m/z 1281.8). Cleavages of the glycosidic bonds yield ceramide-containing Y_j^- product ions at m/z 1119 (Y_3^-), 916 (Y_2^-), 754 (Y_1^-) and a weaker signal at m/z 592 (Y_0^-), thus allowing the determination of sugar sequence. The differences of 162 u, 203 u, 162 u and 162 u correspond to the sequence Hex-HexNAc-Hex-Hex. In addition, ions related exclusively to the carbohydrate portion are observed. The cleavage of the glycosidic bond adjacent to the *N*-acetyl-group is favored and yields the base peak of the product ion spectrum at m/z 916, but the complementary B_2^- fragment is also observed at m/z 364. Furthermore, a fragment corresponding to the complete carbohydrate is observed

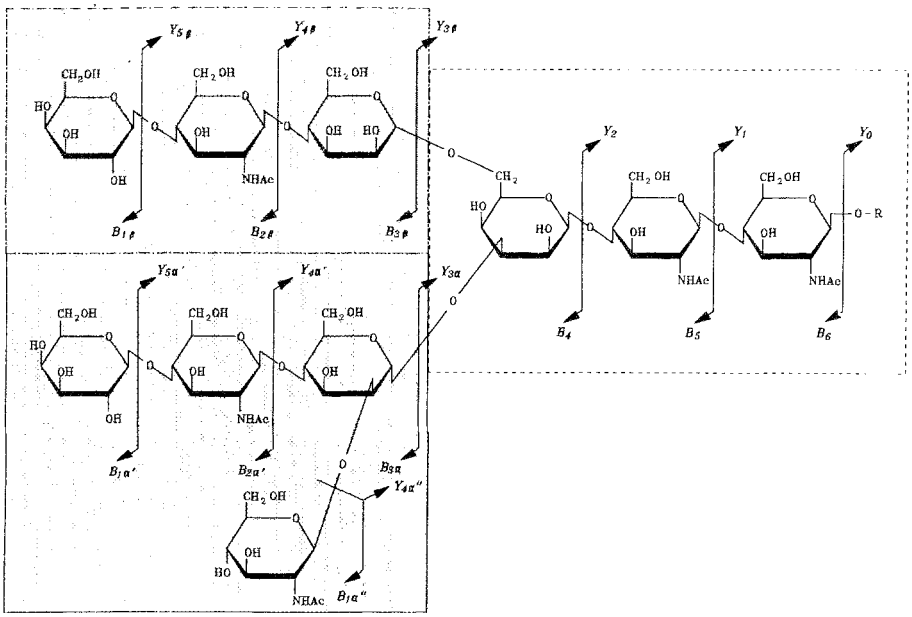

Figure 6. Designations for product ions from a hypothetical branched glycopeptide.

at m/z 706 (C_4^-). A similar ion is observed for the terminal sugar unit at m/z 179 (C_1^-). Fragments resulting from the cleavage within the sugar ring occur at m/z 424 ($[^{2,4}A_3\text{-H}]^-$), 586 ($[^{2,4}A_4\text{-H}]^-$) and 628 ($^{2,5}A_4^-$). Appropriate mass shifts are observed in the CID-MS/MS spectrum of m/z 1253.8, $[M\text{-H}]^-$ of the lower homolog that contains two fewer methylene units in the base (not shown).

Branched Oligosaccharide Moieties

The situation is more complicated in the case of branched oligosaccharides. According to the nomenclature commonly used for glycopeptides and glycoproteins, the carbohydrate portion can be divided into a *"core"* unit and branches, called *"antennae"*. We suggest use of a similar symbol to label the fragments observed in mass spectra. The core refers to the unbranched portion. Each antenna is represented by a Greek letter (α, β, γ), α being the largest; β and γ are assigned with decreasing molecular (fragment) weight, thus $\alpha \geqslant \beta \geqslant \lambda$.

The above nomenclature can thus be extended to branched carbohydrates. Fragmentations taking place on the α- and β-antennae are represented as $A_{i\alpha}$, $B_{i\alpha}$, $C_{i\alpha}$, $X_{j\alpha}$, $Z_{j\alpha}$, respectively. Ions resulting from the *core* unit are designated without a Greek letter, but the numbering begun in the core continues into the antennae, and vice versa. Fig. 5 shows the positive FAB-MS/MS spectrum of a bi-antennary glycopeptide with assignments of the fragments. Because the two antennae are identical in this case, fragments occurring in either chain are observed at the same m/z ratio.

Fragmentation of the glycosidic bond, with loss of the non-reducing terminal portion as a neutral fragment, is observed at m/z 1593 ($Y_{1\alpha}{}^+$ or $Y_{1\beta}{}^+$), 1390 ($Y_{2\alpha}{}^+$ or $Y_{2\beta}{}^+$), 1228 ($Y_{3\alpha}{}^+$ or $Y_{3\beta}{}^+$). The dominant signal at m/z 1390 results from the favored cleavage of the glycosidic bond of the acetamido sugar unit. Ions informative on the carbohydrate portion are observed at m/z 366 ($B_{2\alpha}{}^+$ or $B_{2\beta}{}^+$), characteristic of the *N*-acetyllactosamine moiety. Additional fragments are observed at m/z 528 ($B_{3\alpha}{}^+$ or $B_{3\beta}{}^+$), representing a complete antenna, and m/z 1420 ($B_5{}^+$) resulting from the cleavage between the *N*-acetylglucosamine units.

Further branches, attached to the "primary" antennae are rather common, particularly for glycopeptides. We propose to name these secondary antennae linked to the α- and β-branches α', α'' and β', β''; with $\alpha' \geqslant \alpha''$ and $\beta' \geqslant \beta''$, etc. Fig. 6 exemplifies such a case.

First versus Second Generation Fragments

Fragments resulting from cleavages other than A_i, B_i, C_i, X_j, Y_j and Z_j (first generation fragments, where only one glycosidic bond or sugar ring is involved) have also been observed in FAB-MS and MS/MS spectra. Although they usually look like B_i or Y_j, they in fact result from consecutive fragmentations of two glycosidic bonds. The first one is a regular cleavage yielding a first generation B_i or Y_j ion, which then undergoes another fragmentation to yield a second generation ion.

For glycoconjugates carrying a linear oligosaccharide moiety, first and second generation fragmentations cannot be distinguished because they both yield the same types of products. This is no longer the case for branched oligosaccharide moieties since the two types of ions do not necessarily overlap. Such spectra make an unambiguous sugar sequence determination very difficult, if not impossible. If secondary ions appear to be present in a mass spectrum, a secure interpretation of the spectrum would require the acquisition of an additional mass spectrum under different conditions, where primary ions clearly dominate. This goal may be sometimes achieved by switching from positive to negative ion mode, by varying the collision energy (in the case of MS/MS spectra) or by derivatizing the sample in order to get a compound less prone to undergo subsequent fragmentation.

Nevertheless, it is still useful to have a means of labelling second generation fragments. The above nomenclature is extended to these ions by representing them by a letter followed by a subscript in order to indicate the two glycosidic bonds cleaved ($B_{i/j}$, $Y_{k/l}$ to describe ions which are like B and Y fragments). In addition, the proton transfers have to be specified.

Some second generation fragments are observed in the CID spectrum of the glycopeptide shown in Fig. 5. For example, the signal at m/z 1055 corresponds to the cleavage of the second glycosidic bond (counted from the terminal end) of one of the antennae ($B_{2\alpha}{}^+$ or $B_{2\beta}{}^+$) and the bond linking the two *N*-acetylglucosamine units ($B_5{}^+$). The resulting fragment [Gal-GlcNAc-Man-(Man-)Man-GlcNAc, m/z 1055] would consequently be labelled $B_{2\alpha/5}{}^+$ or $B_{2\beta/5}{}^+$.

A similar redundancy exists for the $Y_{k/l}$ series ions. The peak at m/z 863 represents one of the $Y_{k/l}$ ions (i.e., still containing the aglycone). It results from the cleavage of one of the antennae (3α or 3β) and the *N*-acetyllactosamine moiety of the other one (4α or 4β). That ion could thus be labelled $Y_{3\alpha/4\beta}{}^+$ or $Y_{3\beta/4\alpha}{}^+$. Such situations occur only when a structural unit is repeated; they are still unambiguously defined by the nomenclature.

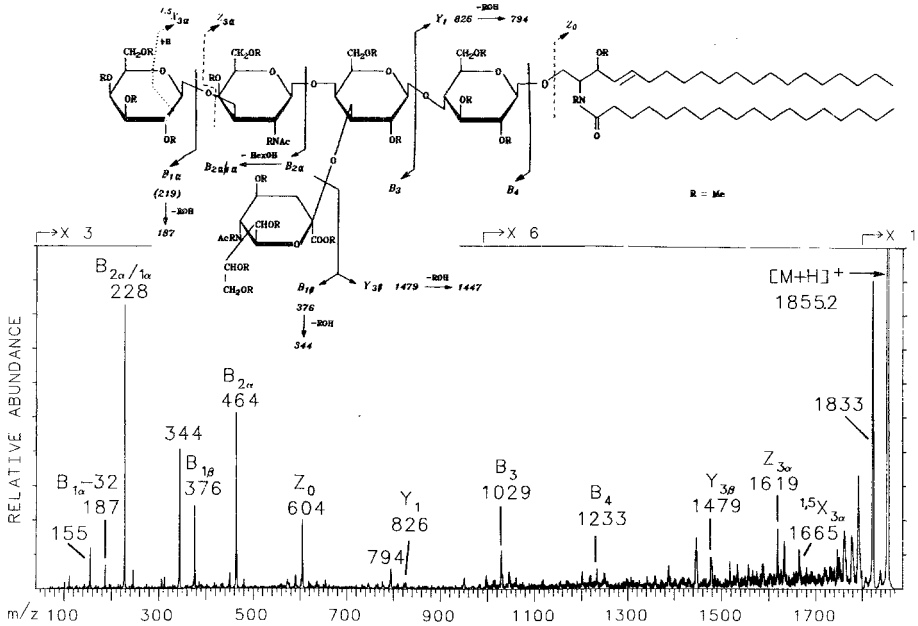

Figure 7. Positive FAB-CID-MS/MS spectrum of permethylated G_{M1}-ganglioside and assignment of product ions; precursor $[M+H]^+$, m/z 1855.2.

Derivatives of Glycoconjugates

Assignments of designations to fragment ions in the spectra of glycoconjugate derivatives proceed according to the rules delineated for native compounds, as illustrated by the positive FAB-CID-MS/MS spectrum of GM1, $[M+H]^+$, m/z 1855.2 (Fig. 7). Some additional fragmentation pathways may be observed when the blocking group can be lost as a stable neutral fragment (e.g. methanol, ketene), or when the derivatization introduces a new site of charge localization (e.g. reduction of an amide to a secondary or tertiary amine). Losses of neutral fragments may be specified by reference to the appropriately named fragment $[(Y_2\text{-}32)^+$ or $(Y_2\text{-MeOH})^+]$. If the named fragment is also present in the spectrum, specific naming of the lost neutral fragment may be unnecessary because of the obvious relationship between the two. Derivatizations within the lipid portion bring about additional fragmentations of the aglycone, as will be discussed elsewhere, but do not introduce new cleavages in the carbohydrate moiety, although the relative abundances of the various fragment types are affected (unpublished data from this laboratory).

The CID-MS/MS spectrum of the $[M+H]^+$ of one of the homologs of permethylated GM1, $[M+H]^+$, m/z 1855.2 (Fig. 7), resembles the FAB-MS spectra reported for a permethylated Fuc-G_{M1}-ganglioside [2] and for permethylated G_{D1a}-ganglioside [21],

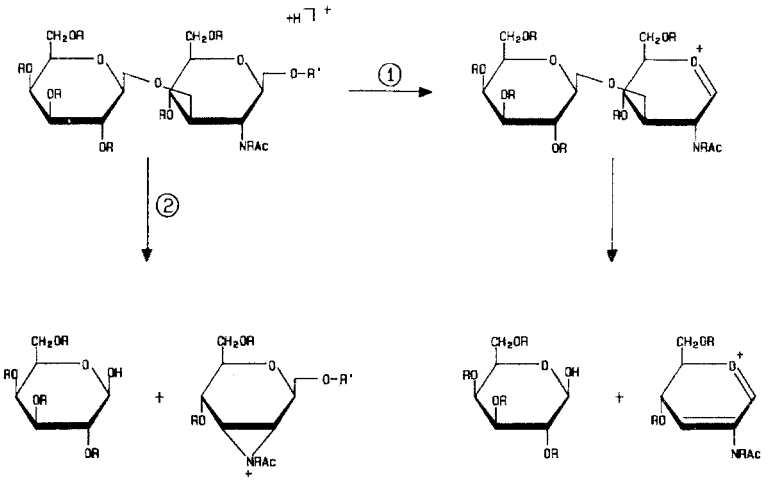

Figure 8. Mechanisms for the elimination of the substituent adjacent to *N*(Me)-acetyl in MS of permethylated glycoconjugates (R = Me).

but it includes more sequence ions and is simpler to interpret because only ions related to one homolog appear in the spectrum. In the CID-MS/MS spectrum, the complete series of B ions is observed, accompanied by sometimes abundant secondary fragments that involve methanol loss [$(B_{1\alpha}\text{-}32)^+$, m/z 187; $(B_{1\alpha}\text{-}64)^+$, m/z 155; $(B_{1\beta}\text{-}32)^+$, m/z 344], as well as loss of hexose ($B_{2\alpha/1\alpha}{}^+$, m/z 228). Elsewhere in the series, the methanol losses are observed, but the peaks have relatively low abundances. Only the $Y_1{}^+$ ion, m/z 826, and $Y_{3\beta}{}^+$ ion, m/z 1479, of the complementary series are present, and for both, the methanol-loss peaks, m/z 794 and m/z 1447, respectively, have higher abundances. Two Z-type are observed: $Z_0{}^+$, m/z 604, the aglycone, and $Z_{3\alpha}{}^+$, m/z 1619, which corresponds to loss of the terminal galactose (above m/z 1500, the fractional mass contributes more than 1 u to the weight, so the values marked on the spectrum and the structure are higher than the nominal mass values). The fragments at m/z 228, 344 and 1619 are all formed by cleavages adjacent to *N*(Me)-acetyl groups. Egge and Peter-Katalinic have pointed out [2] that this type of elimination is characteristic of 3-substituents in the FAB-MS of permethylated glycoconjugates that have 2-*N*(Me)-acetyl groups, and it is likewise observed in EI-MS of the permethylated compounds. Our results indicate that this process is also favored in CID-MS/MS spectra. Observation of the 236 m.u.loss for elimination of the terminal galactose is thus a direct indication that it is linked to the 3-position rather than the 4-position, from which it would have been cleaved in a 218 m.u. loss to form the $Y_{3\alpha}$-ion. Fig. 8 shows a mechanism for this type of elimination along pathways that result in charge retention on (1) the oxonium ion, or (2) the reducing terminus.

One fragment type resulting from ring cleavage accompanied by hydrogen transfer is observed: $[^{1,5}X_{3\alpha}+H]^+$, m/z 1665, and its methanol-loss peak, m/z 1633. Egge and Peter-Katalinic [2] have noted that the $B_4{}^+$ ion (designated D by them) appears only in the FAB-MS spectra of cationized gangliosides, yet in the CID-MS/MS spectrum shown in Fig. 7, it is present as a product ion of $[M+H]^+$.

Conclusion

We have summarized the types of cleavages observed in the collision-induced decomposition MS/MS spectra of glycoconjugates and have described a system for the designation of product ions resulting from cleavages within the carbohydrate moiety in the FAB-MS and MS/MS spectra of glycoconjugates and oligosaccharides. The symbols should be generally useful for both positive and negative ion FAB spectra of natural products and derivatives, and for spectra generated by other ionization modes. Supplementary symbols [4] designate cleavages within the aglycone.

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