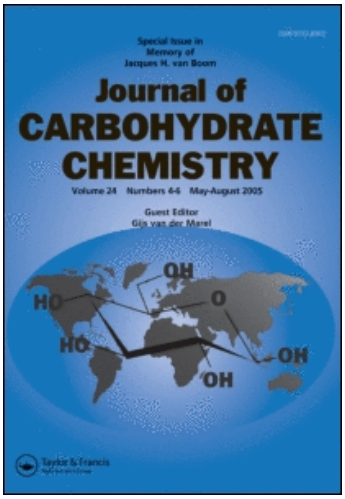


Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Differentiation of Regioisomeric Esters of Sucrose by Ionspray Tandem Mass Spectrometry

Caroline Chauvin[ab]; Pierre Thibault[bc]; Daniel Plusquellec[ab]; Joseph Banoub[bd]

[a] Laboratoire de Chimie Organique et des Substances Naturelles associé au CNRS, Rennes, France [b] Department of Biochemistry, Memorial University of Newfoundland, Canada [c] National Research Council of Canada, Institute for Marine Biosciences, hali, Nova Scotia, Canada [d] Department of Fishenes and Oceans, Science Branch, Canada

To cite this Article Chauvin, Caroline , Thibault, Pierre , Plusquellec, Daniel and Banoub, Joseph(1993) 'Differentiation of Regioisomeric Esters of Sucrose by Ionspray Tandem Mass Spectrometry', Journal of Carbohydrate Chemistry, 12: 4, 459 — 475

To link to this Article: DOI: 10.1080/07328309308019401

URL: http://dx.doi.org/10.1080/07328309308019401

J. CARBOHYDRATE CHEMISTRY, 12(4&5), 459-475 (1993)

DIFFERENTIATION OF REGIOISOMERIC ESTERS OF SUCROSE BY IONSPRAY TANDEM MASS SPECTROMETRY

Caroline Chauvin,[1] Pierre Thibault,[2] Daniel Plusquellec,[1] and Joseph Banoub[3]*

[1]Laboratoire de Chimie Organique et des Substances Naturelles associé au CNRS, École Nationale Superieure de Chimie de Rennes, 35700 Rennes, France
[2]National Research Council of Canada, Institute for Marine Biosciences, Halifax, Nova Scotia B3H 3Z1 Canada
[3]Department of Fisheries and Oceans, Science Branch, P.O. Box 5667, St. John's Newfoundland, Canada A1C 5X1 and Department of Biochemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X9

Received August 20, 1992 - Final Form February 12, 1993

ABSTRACT

Structural characterization and differentiation of distinct regioisomeric esters of sucrose were obtained using ionspray ionization and low energy tandem mass spectrometry. Low energy CAD MS/MS analyses of the protonated molecules $[M + H]^+$ provided characteristic fingerprint patterns, and permitted differentiation of the various regioisomers. MS/MS analyses of selected intermediate fragment ions formed during the ionization process provided additional structural data, and established the fragmentation routes of their $[M + H]^+$ precursors.

INTRODUCTION

Of all the natural sugars used as renewable sources of raw materials, sucrose is the most widespread in nature. Partially acylated sucroses are commercially important compounds which can be used as potential intermediates of significant value for the sucrochemical industry.[1,2] In fact, commercially available sucroesters are now currently

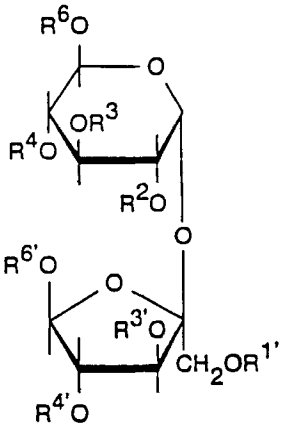
used as emulsifying agents in foods, cosmetics and pharmaceuticals, and as non-ionic detergents for purification of membrane proteins.[3] Although these commercial applications use isomeric mixtures of acylated compounds, there is a constant demand for pure derivatives of sucrose.

Selective monoacylation of sucrose remains at present a quest difficult to achieve, due to the very similar reactivities of the hydroxyl groups[2,4] and to the facile intramolecular acyl migrations occurring in the unprotected derivatives.[4] Nevertheless, some chemical modifications of free sucrose substrate have already been proposed. Indeed, attempts at acylation of the least hindered primary hydroxyl were effected in exceptionally mild conditions,[5] using either sterically hindered reagents or bulky intermediates prepared by the Mitsunobu reaction.[6] Under suitable conditions, these reactions can lead to 6,1',6'-triesters, 6,6'-diesters or 6-monoesters. Recently a selective acylation of the neopentylic-like 1'-OH, by a protease-catalyzed transesterification of sucrose, was reported.[7]

All of these reports indicated that the selective acylation of sucrose remains difficult to achieve, and consequently the synthesis of 6'-*O*-acylsucroses has not yet been achieved successfully. Recently Chauvin and Plusquellec[8] described a new and simple synthesis of 6'-*O*-acylsucroses **1** and **3**, and also succeeded in obtaining high yields of 6-*O*-acylsucrose regioisomers **2** as well as the novel 3-*O*-acylsucrose **4**, from the unprotected sugars (Figure 1). Furthermore, they also reported the syntheses of the 6,6'-di-*O*-acylsucroses using similar conditions.[9] The structural characterization of these well defined regioisomeric esters of sucrose was accomplished using ^{13}C NMR spectroscopy and mass spectrometry. To date, no fast-atom bombardment (FAB) or ionspray (nebuliser-assisted electrospray) mass spectra have been reported for this novel series of regioisomeric esters of sucrose.

Structural information, such as the sequence pattern of oligosaccharide branching[10-13] and differentiation of isomeric hexose units,[14-20] can be obtained by tandem mass spectrometry.[21-22] The unique dissociation patterns of precursor ions provide characteristic fragment ions which facilitate differentiation of isomeric species. Applications of low energy collision-induced dissociation have also been demonstrated for several isomeric peracetylated saccharides,[14-20] anomeric nucleosides,[23-25] *C*-glycosides,[26-29] carbohydrate 1,2-orthocarbonates,[30] and a novel series of diastereoisomeric 1, 2-*trans*-2-deoxy-2-iodoglycosyl azides[31] and phosphoramidates.[32]

In this paper we report the structural characterization and differentiation of the novel series of regioisomer esters of sucrose using ionspray mass spectrometry.[33] Structural



1: R^2=R^3=R^4=R^6=$R^{1'}$=$R^{3'}$=$R^{4'}$=H; $R^{6'}$=$CO(CH_2)_6CH_3$

2: R^2=R^3=R^4=$R^{1'}$=$R^{3'}$=$R^{4'}$=$R^{6'}$=H; R^6=$CO(CH_2)_6CH_3$

3: R^2=R^3=R^4=R^6=$R^{1'}$=$R^{3'}$=$R^{4'}$=H; $R^{6'}$=$CO(CH_2)_3C_6H_5$

4: R^2=R^4=R^6=$R^{1'}$=$R^{3'}$=$R^{4'}$=$R^{6'}$=H; R^3=$CO(CH_2)_3C_6H_5$

Figure 1. Structures of the different regioisomeric esters of sucrose **1** - **4**.

information was also deduced from low energy tandem mass spectral analysis of the protonated molecules $[M + H]^+$. Rationalization of the fragmentation routes was made by obtaining the product and precursor ion spectra of the various intermediate ions.

RESULTS AND DISCUSSION

Fast atom bombardment (FAB) ionization has been shown to be a useful ionization technique for the analysis of a wide range of natural compounds, including carbohydrates.[34] FAB-MS spectra of carbohydrates are usually characterized by abundant $[M + H]^+$ and $[M + Na]^+$ ions, thus permitting molecular mass determination. In addition, fragment ions enable deduction of structural information. However, the low abundance of fragment ions and the chemical noise resulting from matrix ions can limit the sequence information that one can deduce from the mass spectrum. Early attempts to obtain structural information on this novel series of regioisomeric esters of sucrose using FAB-MS were confusing and not conclusive.[35] For example, FAB-MS analyses of

6'-*O*-octanoylsucrose **1** and 6-*O*-octanoylsucrose **2** did not show the presence of the expected protonated molecules $[C_{20}H_{36}\ 0_{12}+ H]^+$, and only minute traces (<1%) of the sodiated adduct ions $[C_{20}H_{36}\ 0_{12} + Na]^+$ were observed. Furthermore, ions corresponding to the protonated molecules of di-*O*-octanoyl- and tri-*O*-octanolysucroses, ($[C_{28}H_{50}0_{13} + H]^+$ and $[C_{36}H_{64}0_{14} + H]^+$ respectively), were observed in the FAB-MS analysis of **1** and **2**. Fragment ions derived from these latter two protonated molecules were also observed in the FAB mass spectra. Obviously, these results could only cast doubt on the structural assignment of the 6'-*O*-octanoyl- and 6-*O*-octanoylsucroses **1** and **2**. The formation of protonated molecules of the diacylated and triacylated sucroses could possibly be explained by intermolecular reactions, between the acylating ions ($CH_3\ (CH_2)_6CO^+$) and the original 6'-*O*-octanoyl- or 6-*O*-octanoylsucrose molecule, in either the gaseous phase or in the liquid matrix.

The ionspray MS of the regioisomers 6'-*O*-octanoylsucrose **1** and 6-*O*-octanoylsucrose **2** are shown in Figure 2, and are summarized in Table 1. In contrast to the rather deceiving FAB-MS results, the ionspray mass spectra of these two regioisomers gave abundant protonated molecules $[M + H]^+$ as well as an adduct corresponding to $[M + H + CH_3OH]^+$. Sodiated and ammoniated adducts respectively at m/z 491 and 486 were observed only for regioisomer **1**.

A cursory glance at Figure 2 and Table 1 indicates that these two regioisomers give distinct spectra, with different relative abundances for common fragment ions. For the two regioisomers, the $[MH + MeOH]^+$ protonated molecule-solvent adduct ions at m/z 501 and the protonated molecules $[M + H]^+$ at m/z 469, appear at very different relative abundances. The fragmentation routes of these regioisomers have been rationalized using the scheme for systematic nomenclature for carbohydrate fragmentation in FAB-MS proposed by Domon and Costello.[36] In this rationale the fragmentation routes yielding fragments B and C occur by simple cleavage of the protonated glycosidic bond, leading to fragment ions containing the terminal glucopyranosyl unit. Alternatively, the fragmentation routes giving rise to fragments Y and Z involve a different cleavage of the protonated glycosidic bond, and form fragment ions containing the fructofuranosyl unit. It should also be mentioned that formation of the fragment ions $[C]^+$ and $[Y]^+$ involve H-transfers with concurrent cleavage of the protonated glycosidic bond.[13,36]

A summary of the proposed modes of formation, and suggested structures, of the fragment ions formed during the dissociation of the protonated molecular ions $[M + H]^+$

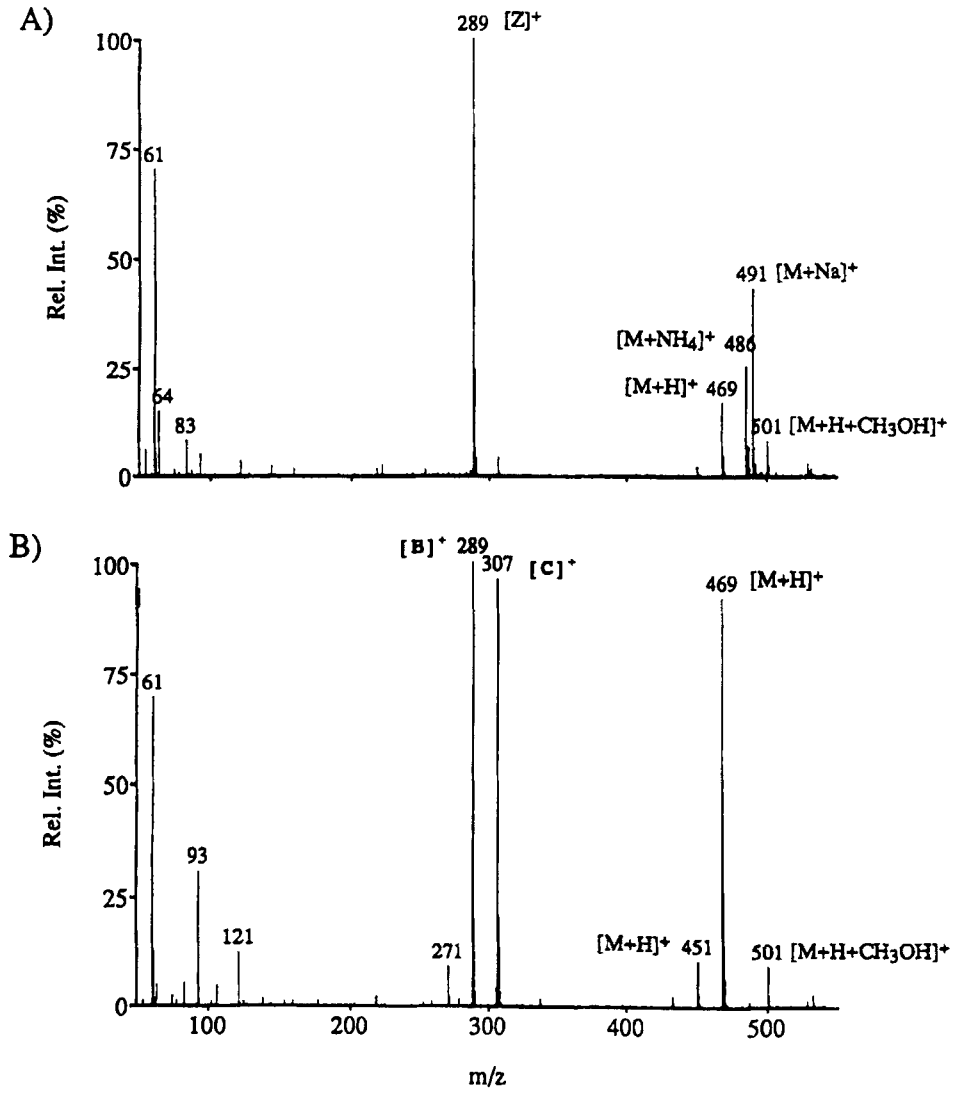


Figure 2. Positive ionspray mass spectra of the 6'-*O*-octanoylsucrose **1** (A) and 6-*O*-octanoylsucrose **2** (B).

(m/z 469) for 6'-*O*-octanoyl- and 6-*O*-octanoylsucroses **1** and **2** are shown in Figures 3 and 4.

Low energy tandem mass spectrometric analyses were conducted to rationalize the fragmentation pathways leading to the various fragment ions observed in the conventional ionspray MS (see Table 1). Product ion spectra, arising from fragmentation in the RF-

Table 1. Characteristic ions in the ionspray mass spectra of the regioisomers 6'-*O*-octanoylsucrose **1** and 6-*O*-octanoylsucrose **2** [$C_{20}H_{36}0_{12}$, MW = 468].

Characteristic Ion	m/z	6'-*O*-octanoylsucrose **1**		6-*O*-octanoylsucrose **2**	
		Ion Type	Rel. Int.	Ion Type.	Rel. Int.
$[MH+MeOH]^+$	501	-	7.5	-	7
$[M+Na]^+$	491	-	39	-	-
$[M+NH_4]^+$	486	-	26	-	-
$[M+H]^+$	469	-	15	-	89
$[MH-H_20]^+$	451	-	-	-	10
$[MH-162]^+$	307	-	-	$[C]^+$	97
$[MH-180]^+$	289	$[Z]^+$	100	$[B]^+$	100
$[MH-180-H_20]^+$	271	$[Z-H_20]^+$	-	$[B-H_20]^+$	9

Table 2. Low energy CAD MS/MS spectra of the precursor ions $[M + H]^+$ at m/z 469 obtained from the two regioisomers, 6'-*O*-octanoylsucrose **1** and 6-*O*-octanoylsucrose **2**.

Characteristic Ion	m/z	6'-*O*-octanoylsucrose **1**		6-*O*-octanoylsucrose **2**	
		Ion Type	%	Ion Type	%
$[MH-162]^+$	307	$[Y]^+$	6	$[C]^+$	83.3
$[MH-180]^+$	289	$[Z]^+$	100	$[B]^+$	100
$[MH-180-H_20]^+$	271	$[Z-H_20]^+$	3	$[B-H_20]^+$	17
$[MH-180-2H_20]^+$	253	-	-	$[B-2H_20]^+$	3
$[MH-306]^+$	163	-	-	$[Z]^+$	5
$[MH-306-H_20]^+$	145	-	-	$[Z-H_20]^+$	7
$[MH-306-2H_20]^+$	127	-	-	$[Z-2H_20]^+$	5

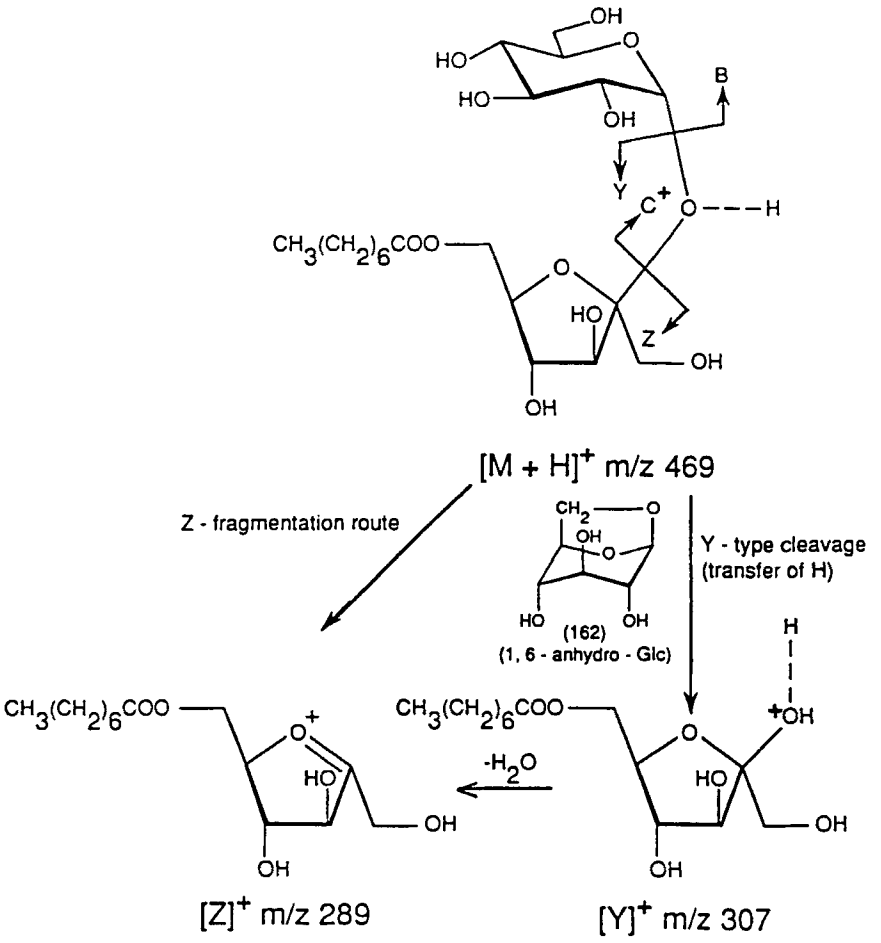


Figure 3. Major fragmentation routes of the $[M + H]^+$ ion of 6'-*O*- octanoylsucrose observed by ionspray MS and CAD MS/MS. The Y-type cleavage was observed only in the MS/MS spectrum of the precursor $[M + H]^+$ ion.

only quadrupole collision cell of the triple-quadrupole instrument, were obtained. The low energy CAD MS/MS spectra for the $[M + H]^+$ ions, obtained for the regioisomers 6'-*O*-octanoyl- and 6-*O*-octanoylsucroses **1** and **2**, are summarized in Table 2 and tentatively depicted in Figures 3 and 4. Comparisons between these two sets of data show distinct differences between the relative abundances of the common fragment ions. For example the CAD MS/MS of the $[M + H]^+$ ion of 6-*O*-octanoylsucrose **2** suggests three different fragmentation pathways as depicted in Figure 4. The first pathway occurs via loss of anhydrofructose (162 Da) to form the product ion $[C]^+$ at m/z 307. Formation

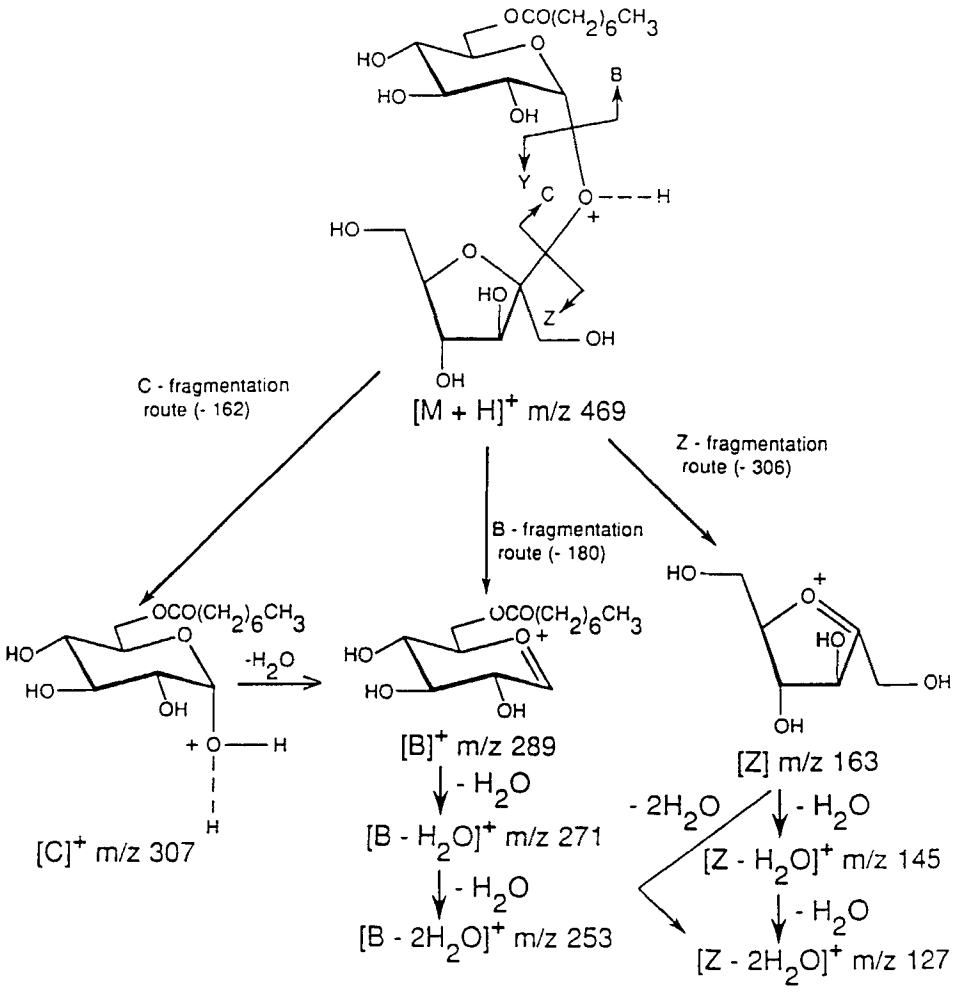


Figure 4. Major fragmentation routes of the $[M + H]^+$ ion of 6-*O*- octanoylsucrose observed by ionspray MS and CAD MS/MS. The Z fragmentation route was not observed in the MS spectrum but was obtained in the CAD MS/MS spectra of the precursor $[M + H]^+$ ion.

of the B-type ion arises from cleavage of the glycosidic bond, to afford the fragment ion at m/z 289 which subsequently loses one and two molecules of H_20 giving the fragment ions at m/z 271 and 253, respectively. Finally, the third pathway occurs via the loss of 6-*O*-octanoylglucose (306 Da) to yield the reducing oxonium ion $[Z]^+$ at m/z 163. This latter ion may successively lose two molecules of water, to give the fragment ions at m/z 145 and 127. It is noteworthy that the ions at m/z 163, 145, and 127 are specific to 6-*O*-octanoylsucrose **2**, whereas no such fragment ions are observed in the case of 6'-*O*-octanoylsucrose **1**.

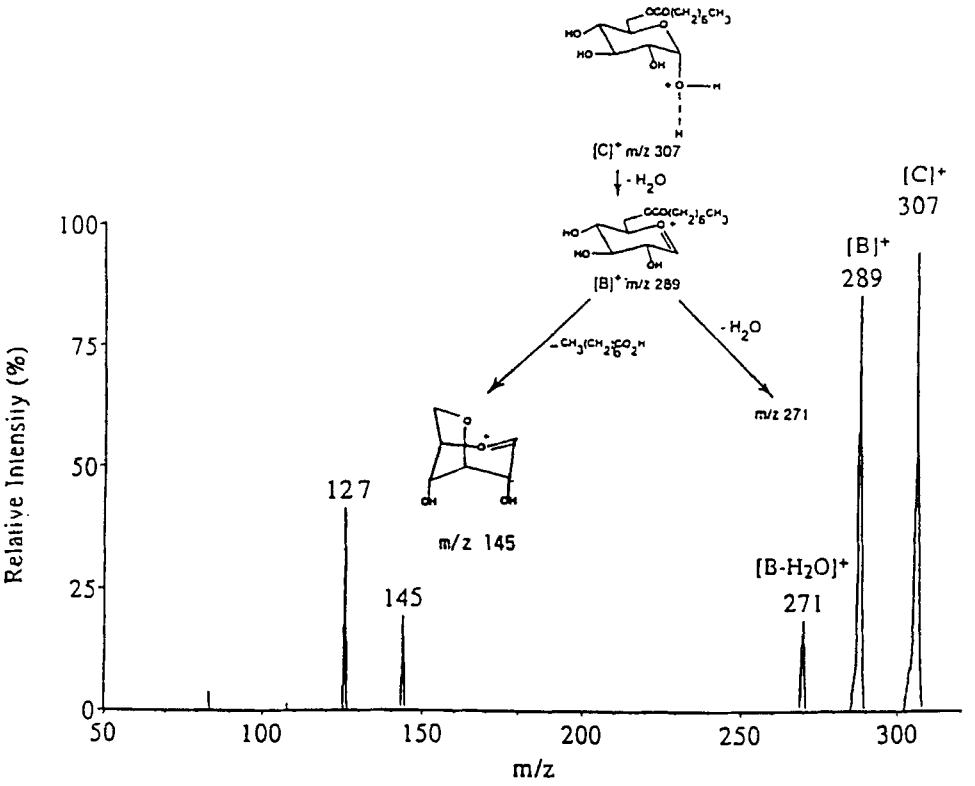


Figure 5. MS/MS spectrum of the intermediate ion m/z 307 from 6-*O*-octanoyl-D-glucose formed in the ionspray source. Conditions: Argon target gas, gas thickness 3 X 10^{14} atoms/cm^2, laboratory frame collision energy 100eV.

Interestingly the product ion $[B]^+$ at m/z 289 could originate from two different processes, either by simple cleavage resulting from the B-type fragmentation route, or more likely by a two-step process involving loss of water from the intermediate product ion $[C]^+$ at m/z 307. Second-generation product ions of intermediate fragment ions formed during the ionization process, were generated in an MS/MS experiment and permitted confirmation of this latter $[C]^+$ intermediate possibility. The intermediate fragment ion at m/z 307 can lose a molecule of water to afford the ion $[B]^+$ at m/z 289, which fragments further to form the ions at m/z 271, 145 and 127 as shown in Figure 5.

In a different set of experiments, the precursor ions of the $[B - H_20]^+$ ion at m/z 271 were sought using the precursor ion scan technique. It was thus established that the ion at m/z 271 originates from the $[C]^+$ and $[B]^+$ intermediate ions, at m/z 307 and 289, respectively, as shown in Figure 6. Also the product ion $[C]^+$ at m/z 307 might lose two

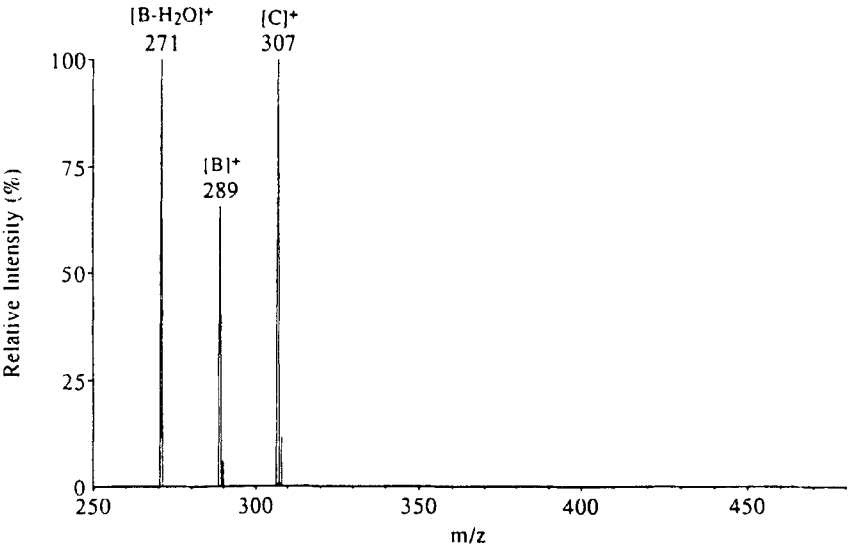


Figure 6. Parent ion scan of m/z 271 from 6-*O*-octanoyl-D-glucose. Conditions as for Figure 5.

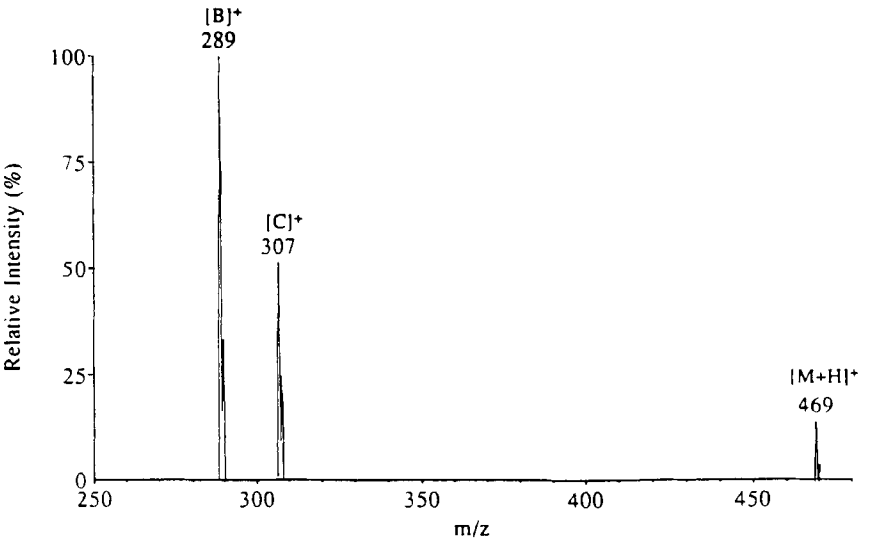


Figure 7. Parent ion scan of m/z 289 from 6-*O*-octanoyl-D-glucose. Conditions as for Figure 5.

Table 3. Characteristic ions in the ionspray mass spectra of the regioisomeric 6'-*O*-phenylbutyrylsucrose **3** and 3-*O*-phenylbutyrylsucrose **4**

Characteristic Ion	m/z	6'-*O*-phenylbutyrylsucrose **3**		3-*O*-phenylbutyrylsucrose **4**	
		Ion Type	%	Ion Type	%
$[MH+MeOH]^+$	521	-	9	-	13
$[M+Na]^+$	511	-	67	-	23
$[M+NH_4]^+$	506	-	31	-	25
$[M+H]^+$	489	-	22	-	24
$[MH-162]^+$	327	$[Y]^+$	5	$[C]^+$	100
$[MH-180]^+$	309	$[Z]^+$	100	$[B]^+$	51

Table 4. Low energy CAD MS/MS spectra of the precursor ions $[M + H]^+$ at m/z 489, for the regioisomer 6'-*O*-phenylbutyryl and 3-*O*-phenylbutyrylsucrose **3** and **4**.

Fragment Ion	m/z	6'-*O*-phenylbutyrylsucrose **3**		3-*O*-phenylbutyrylsucrose **4**	
		Ion Type	%	Ion Type	%
$[MH-162]^+$	327	$[Y]^+$	5	$[C]^+$	100
$[MH-180]^+$	309	$[Z]^+$	100	$[B]^+$	83
$[MH-180-H_2O]^+$	291	$[Z-H_2O]^+$	3	$[B-H_2O]^+$	5

molecules of water simultaneously by a concerted mechanism. This possibility has not been studied further as it is beyond the scope of the present work. In a similar experiment it was shown that the product ion $[B]^+$ at m/z 289 can indeed be formed either from the intermediate ion $[C]^+$ or directly from the precursor $[M + H]^+$, as shown in Figure 7. In this context, note that "concerted loss" of 2 H_2O, in the MS-MS experiment, simply means they are both lost within the time-window of the same reaction region within the tandem mass spectrometer. No conclusions about "concerted" reactions on the molecular timescale can be drawn.

In a similar fashion the regioisomers 6'-*O*-phenylbutyrylsucrose **3** and 3-*O*-phenylbutyrylsucrose **4** were also studied by ionspray mass spectrometry. The

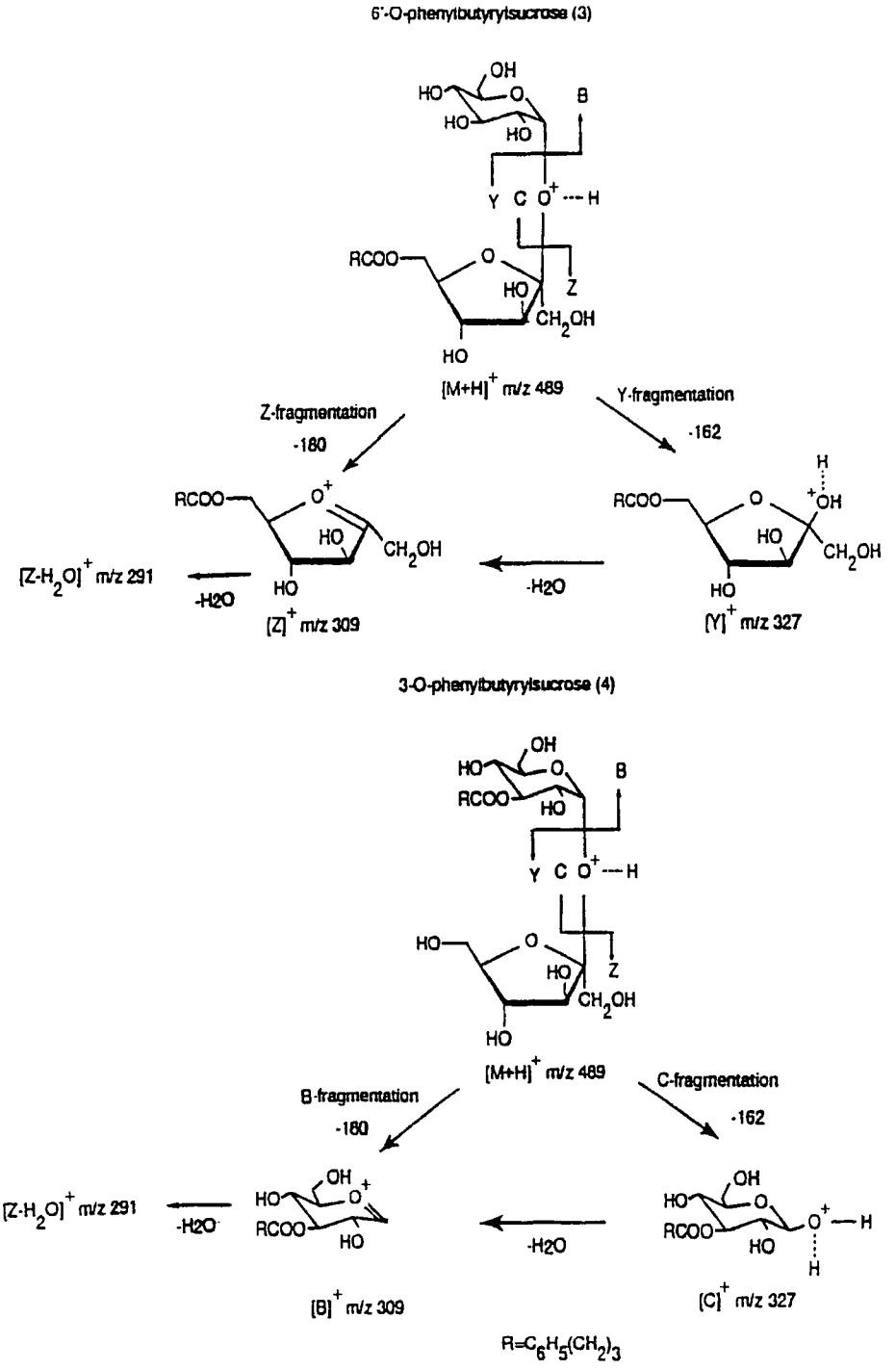


Figure 8. Major fragmentation routes for the $[M + H]^+$ ions of 3-*O*-phenylbutyrylsucrose 4 and 6'-*O*-phenylbutyrylsucrose 3 observed by Ionspray CAD MS/MS.

characteristic ions obtained for this pair of regioisomers are presented in Table 3. Comparison of these data shows very different fragment spectra for these two isomers. These two regioisomers afford the molecule-solvent adduct $[MH + MeOH]^+$ as well as $[M + NH_4^+]$, at m/z 521 and 506, respectively. The protonated molecules $[M + H]^+$ and sodiated adducts $[M + Na]^+$ at m/z 489 and 511, respectively, were obtained in different relative abundances for these two isomers.

Low energy tandem mass spectrometry was also conducted for the regioisomers **3** and **4** to rationalize their fragmentation patterns. The low energy CAD MS/MS spectra for the $[M + H]^+$ ions of these two compounds are summarized in Table 4. Examination of Table 4 reflects characteristic differences in their relative abundances of common fragment ions, thus facilitating differentiation of this pair of regioisomers. Proposed fragmentation patterns for the $[M + H]^+$ precursor ions at m/z 489, which rationalize the observed MS-MS spectra, are presented schematically in Figure 8. The dissociation of the $[M + H]^+$ precursor ion, for the 6'-*O*-phenylbutyrylsucrose **3** may occur via the Y-type fragmentation route by elimination of the anhydroglucose moiety (162 Da) to afford the $[Y]^+$ fragment ion at m/z 327. This ion can subsequently lose a molecule of water yielding the fragment ion $[Z]^+$ at m/z 309. Similarly Z-type cleavage, which occurs by the loss of a terminal reducing glucosyl unit (180 Da), gives rise to the fragment ion $[Z]^+$ at m/z 309 which loses a molecule of water to afford the $[Z\text{-}H_20]^+$ fragment ion at m/z 291. Fragmentation patterns of protonated 3-*O*-phenylbutyrylsucrose **4** involve two different routes, contrary to the case of the 6'-*O*-phenylbutyrylsucrose **3**. Fragmentation of the $[M + H]^+$ ion of **4** via C-type cleavage, with elimination of a molecule of anhydrofructose (162 Da), affords the $[C]^+$ fragment ion at m/z 327, which subsequently loses a molecule of water to give the $[B]^+$ fragment ion at m/z 309. Similarly, B-type cleavage may occur with hydrogen transfer to the terminal reducing fructosyl unit (180 Da), resulting in the formation of the $[B]^+$ fragment ion at m/z 309.

As with the other members of this novel series of regioisomers the alkyl chain substituent, whether located on the 6-0-, 6'-0- or 3-0- positions, seems to direct the fragmentation routes. Fragment ions comprising the alkyl chain substituent are generally of greater abundance thus suggesting the participation of the alkyl chain in the stabilisation of the positively charged fragment.

CONCLUSIONS

Mass spectral analyses of regioisomeric esters of sucrose have been facilitated using ionspray ionization. Abundant signals corresponding to protonated, sodiated and ammoniated adducts of the derivatized sucrose molecules were observed in all cases using this ionization technique. In contrast, the FAB-MS spectra of the same compounds did not provide any conclusive information concerning either their molecular weights or their isomeric structures.

MS/MS spectra of the regioisomeric sucrose esters, obtained using low energy collisional activation, permitted differentiation of the various isomers. Fragmentation of the octanoylsucroses was highly influenced by the position of the alkyl chain within the carbohydrate structure. For example the MS/MS spectrum of the $[M + H]^+$ ion of the 6'-*O*-octanoylsucrose yields a major Z-type fragment ion, whereas the corresponding spectrum of the 6-*O*-octanoylsucrose was dominated by B-type and C-type fragment ions at m/z 289 and 307, respectively. The fragmentation patterns observed in the MS/MS spectra of the various sucrose ester derivatives reflects the differences in their chemical structures. The distinct MS/MS spectra obtained for these compounds permitted differentiation of the various regioisomers. Furthermore parent ion scans, and MS/MS spectra of selected intermediate ions formed during the ionization process, permitted rationalization of the fragmentation behaviour.[37]

EXPERIMENTAL

Compounds and Sample Preparation:

Synthesis of the octanoyl and phenylbutyrylsucrose derivatives was accomplished according to previous methods.[8,9] The purified sucrose derivatives were dissolved in 50% methanol (BDH Chemicals, Poole, UK), 0.1% formic acid (Fisher Scientific, Raleigh, NC, USA) and 50% distilled and deionized water (Milli-Q water systems, Millipore Inc., Bedford, MA, USA). Solutions of 1mg/mL of derivatives were prepared prior to mass spectral analysis.

Mass Spectrometry.

A ZAB-EQ hybrid tandem mass spectrometer (VG Analytical, Manchester, U.K.) equipped with a VG 11-250J Data System, was used for all LSIMS analyses of the sucrose ester derivatives. Approximately 2μg of sample was deposited on a gold tipped probe and dissolved in 3μL of the matrices glycerol or 3-nitrobenzyl alcohol. A Cs^+ gun

(VG Analytical, Manchester, UK) operating at 30keV was used for the LSIMS ionization. Conventional mass spectra were obtained by scanning the mass spectrometer from 50 to 1000 Da in 10s. Ionspray mass spectra were obtained using an API III triple quadrupole mass spectrometer (SCIEX, Thornhill, Ontario, Canada) equipped with an atmospheric pressure ionization (API) source operated in the ionspray mode. A MacIntosh IIX computer was used for data acquisition and data processing. Samples were introduced to the mass spectrometer by infusing a solution at a flow rate of 5μL/min. The voltage of the ionspray needle was maintained at 5kV, while the orifice voltage was typically 100V. A 0.6L/min flow of high purity air was used as nebulizing gas.

Tandem mass spectrometry experiments used the API III instrument. Fragment ion spectra of mass-selected ions were induced by collisions with argon in the second (RF only) quadrupole. The resulting fragments were mass analyzed by the third quadrupole. The target thickness was typically 3 X 10^{14} atoms cm^{-2} and collision energies of approximately 100eV (laboratory frame) were used in all MS/MS experiments. Precursor ions scans were obtained by scanning the first quadrupole while selecting a given m/z value with the third quadrupole.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. R. K. Boyd for helpful discussions and reviewing the manuscript. The assistance of Mrs. R. MacArthur, Mrs. P. Blay and Mr. H. Hodder in the preparation of the manuscript is also gratefully acknowledged.

REFERENCES AND NOTES

1. Presented at the *XVIth International Carbohydrate Symposium*, Paris, France, July 5-10, 1992.
2. R. Kahn, *Pure Appl. Chem.*, **56**, 883 (1984).
3. H. Schiweck, K. Rappand and M. Vogel, *Chem. & Ind.*, 228(1988).
4. A. H. Haines, *Adv. Carbohydr. Chem. Biochem.*, **33**, 11 (1976).
5. M. S. Chowdhary, L. Hough and A. C. Richardson, *J. Chem. Soc. Perkin Trans. I.*, **3**, 419 (1984).
6. O. Mitsunobu, *Synthesis*, 1 (1981); S. Bottle and I.D. Jenkins, *J. Chem. Soc. Chem. Commun.* 385(1984)

7. S. Riva, J. Chopineau, A. P. G. Kieboom and A. M. Klibanov, *J. Am. Chem. Soc.*, **110**, 584 (1988).

8. C. Chauvin and D. Plusquellec, *Tetrahedron Lett.*, **32**, 3495 (1991).

9. C. Chauvin, K. Baczko and D. Plusquellec, Presentation at the 2nd International Workshop on Carbohydrates as Raw Materials, Lyon (FRANCE) July 1992, *Zucker Ind.*, **117**, 476 (1992).

10. Z. Zhou, S. Ogden, J. A. Leary, *J. Org. Chem.*, **55**, 5444 (1990).

11. R. A. Laine, K. M. Pamidimukkala, A. D. French, R. W. Hall, S. A. Abbas, R. K. Jain, K. L. Matta, *J. Am. Chem. Soc.*, **110**, 6931 (1988).

12. J. W. Dallinga, W. Heerma, *Biol. Mass Spectrom.*, **20**, 99 (1991).

13. B. Domon, J. E. Vath, C. E. Costello, *Anal. Biochem.*, **184**, 151 (1990).

14. W. J. Richter, W. Blum, U. P. Schlunegger and M. Senn in *Tandem Mass Spectrometry*; F. W. McLafferty, Ed.; Wiley: New York, 1983, p 417.

15. R. Guevremont and J. L. C. Wright, *Rapid Comm. Mass Spectrom.*,**1**, 12 (1987).

16. D. R. Mueller, B. M. Domon, W. Blum, F. Raschdorf and W. J. Richter, *Biomed. Env. Mass Spectrom.*, **15**, 441 (1988).

17. A. Ballistreri, G. Montaudo, D. Garozzo, M. Giuffrida and G. Impallomeni, *Rapid Comm. Mass Spectrom.*, **3**, 302 (1989).

18. B. Domon, D. R. Müller and W. J. Richter, *Org. Mass Spectrom.*, **24**, 357 (1989).

19. R. Guevremont, V. P. Pathak and J. L. C. Wright, *Org. Mass Spectrom.*, **25**, 101 (1990).

20. G. Puzo, J. C. Prome and J. J. Fournie, *Carbohydr. Res.*, **140**, 131 (1985).

21. *Tandem Mass Spectrometry*; F. W. McLafferty, Ed.; Wiley-Interscience: New York, 1983.

22. *Mass Spectrometry/Mass Spectrometry*; K. L. Busch, G. L. Glish and S. A. McLuckey, Eds.; VCH: New York, 1988.

23. J. Banoub, G. MacKenzie, G. Descotes, R. W. Humble, G. Shaw, M. Becchi and D. Fraisse, *Biomed. Environ. Mass Spectrom.*, **19**, 97 (1990).

24. J. Banoub, M. Becchi, G. Descotes, D. Fraisse, R. W. Humble and G. MacKenzie, *Spectroscopy*, **9**, 79 (1991).

25. J. Banoub, M. Becchi, G. Descotes, D. Fraisse, R. W. Humble and G. MacKenzie, *J. Carbohydr. Chem.*, **11**, 471 (1992).

26. M. Brakta, P. Lhoste, D. Sinou and J. Banoub, *Carbohydr. Res.*, **203**, 148 (1990).

27. M. Brakta, P. Lhoste, D. Sinou, M. Becchi, M. Fraisse and J. Banoub, *Org. Mass Spectrom.*, **25**, 249 (1990).

28. M. Brakta, B. Chaguir, D. Sinou, J. Banoub and M. Becchi, *Org. Mass Spectrom.*, **27**, 331 (1992).

29. M. Brakta, D. Sinou, M. Becchi and J. Banoub, *Org. Mass Spectrom.*, **27**, 621 (1992).

30. E. Gentil, J. Banoub, P. Boullanger and F. Delorme, *Org. Mass Spectrom.*, **25**, 124 (1990).

31. J. Banoub, M. Becchi, D. Lafont, D. Fraisse and G. Descotes, *Rapid Commun. Mass Spectrom.*, **4**, 536 (1990).

32. J. Banoub, D. Lafont, M. Becchi, D. Fraisse and G. Descotes, *Spectroscopy*, **10**, 71 (1992).

33. T. R. Covey, R. F. Bonner, B. I. Shushan and J. Heniou, *Rapid Commun. Mass Spectrom.*, **249**, (1988).

34. A. Dell, *Adv. Carbohydr. Chem. Biochem.*, **45**, 19 (1987).

35. C. Chauvin, P. Thibault, D. Plusquellec and J. Banoub, unpublished results.

36. B. Domon and C. E. Costello, *Glycoconjugate J.*, **5**, 397 (1988).

37. This publication has been assigned NRCC#.34817.