Carbohydrate Research, 115 (1983) 95–104
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CLEAVAGE OF INTERGLYCOSIDIC LINKAGES IN PER(TRIMETHYLSILYL)ATED AND PERMETHYLATED CARBOHYDRATES WITH IODOTRIMETHYLSILANE

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(Received June 15, 1982; accepted for publication, July 12th, 1982)

ABSTRACT

Iodotrimethylsilane in carbon tetrachloride cleaves interglycosidic linkages in per(trimethylsilyl)ated disaccharides to give iodinolysis products that may be readily hydrolyzed to component monosaccharides. The cleavage rate is dependent on the type of interglycosidic linkage, and is in the order (1→4) < (1→2) < (1→3) < (1→6) for derivatives of β-linked glucobioses. This iodinolysis reagent is more reactive toward interglycosidic linkages in permethylated carbohydrates; all of the linkages in the permethylated derivatives examined were completely cleaved, irrespective of linkage type. Iodinolysis with iodotrimethylsilane, followed by treatment of the products with water, offers a rapid and mild method for hydrolysis of permethylated carbohydrates.

INTRODUCTION

Iodotrimethylsilane (ITMS) is a recently developed synthetic reagent that catalyzes a variety of important reactions, such as cleavage of ether[1] and ester[2] linkages, as well as conversion of ketals into ketones[3]. It also catalyzes the reduction of alkyl carbamates to amines[4] and that of sulfoxides to sulfides[5]. With carbohydrates, Thiem and Meyer[6] reported that the reactions of peracetylated mono- and di-saccharides with ITMS affords high yields of peracetylated glycosyl iodides. Under their conditions, the interglycosidic linkages were not affected. Recently, however, we found that interglycosidic linkages in per(trimethylsilyl)ated and permethylated oligosaccharides are readily cleaved with ITMS under milder conditions, in contrast to those in peracetylated oligosaccharides. As the iodinolysis products may be rapidly and quantitatively hydrolyzed to free and partially methylated monosaccharides, respectively, the iodinolytic cleavage with this reagent may lead to a novel method for hydrolysis of carbohydrate chains. This paper describes the results of optimization studies of the ITMS method, and presents some preliminary applications.

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0008-6215/83/$ 03.00

EXPERIMENTAL

General methods. — All evaporations were performed under diminished pressure below 40°.

Materials. — Iodo- and bromo-trimethylsilanes were obtained from Aldrich Chemicals (Milwaukee, Wisconsin); chlorotrimethylsilane was purchased from Tokyo Kasei Kogyo (Toshima, Kita-ku, Tokyo). All other chemicals, solvents, and the samples of free carbohydrates were of the highest grade commercially available. The samples of per(trimethylsilyl)ated mono- and di-saccharides were prepared by per(trimethylsilyl)ation of the parent carbohydrates with chlorotrimethylsilane and hexamethyldisilazane in pyridine, according to the literature[7]. The mixtures were evaporated to dryness, and the residues were extracted with chloroform. The chloroform extracts were washed with iced water and evaporated to dryness. The derivatives of monosaccharides were further purified by distillation under diminished pressure; those of disaccharides were used without distillation. Authentic specimens of permethylated mono- and disaccharides were obtained by methylation of the parent carbohydrates by the method of Hakomori[8], followed by purification of the products on columns of Wakogel C-200 with 30 : 1 chloroform–methanol as solvent. All of these specimens gave single peaks on gas chromatography. Solvents were dehydrated by conventional methods (carbon tetrachloride, chloroform, and nitromethane with calcium chloride; acetonitrile with phosphorus pentaoxide; pyridine with sodium hydroxide; and dimethyl sulfoxide with molecular sieve 4A), and distilled before use.

Apparatus. — Gas chromatography was performed on a Shimadzu 4BMPF instrument equipped with a hydrogen flame-ionization detector. Analyses of dithioacetal derivatives of free and partially methylated monosaccharides were performed by using a Scot capillary column (0.28 mm i.d., 50 m) coated with silicone SF-96 at 225°, according to the literatures[9,10]. Other gas-chromatographic analyses were performed by using a glass column (3 mm i.d., 1 m) packed with Chromosorb W (AW-DMCS, 80–100 mesh) coated with 2% silicone OV-1 at 190°. The flow rates of the carrier (nitrogen for both columns) were controlled at 1 and 30 mL·min, respectively. Gas chromatography–mass spectrometry was performed with a Hitachi M-70 spectrometer by using an OV-1 column. The ionization potential of the mass spectrometer was 70 eV, and the column conditions were the same as those already described.

*Iodinolysis of methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-*D*-glucopyranoside.* — A sample of methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside (1 μmol) was dissolved in carbon tetrachloride (100 μL), and ITMS (20 μL) was added. The solution was kept for 30 min at 25°. One-μL aliquots were removed and analyzed by g.c. and g.l.c.–m.s. Methanol (50 μL) and silver oxide (10 mg) were then added to the remaining portion of the mixture, which was then stirred for 30 min at room temperature. The solvent was evaporated, and the residue dissolved in pyridine (50 μL). Hexamethyldisilazane (100 μL) and chlorotrimethylsilane (50 μL) were then added, and the mixture was incubated for 30 min at 50°. The mixture was

centrifuged, and a 1-μL-sample of the supernatant solution was analyzed by gas chromatography.

Another iodinolysis reaction-mixture, obtained by the same procedure, was diluted with carbon tetrachloride (300 μL), and the resultant solution was shaken thrice with iced water (500 μL). The combined aqueous layers were introduced onto a column containing Amberlite CG-400 (acetate form, 1 mL), and the column was washed with water (30 mL). The combined eluate and the washings were evaporated to dryness, and the residue was dissolved in pyridine (50 μL). Hexamethyldisilazane (100 μL) and chlorotrimethylsilane (50 μL) were added, and the mixture was incubated for 30 min at 50°. The mixture was centrifuged, and a 1 μL-sample of the supernatant solution was analyzed by gas chromatography.

All gas-chromatographic analyses were performed on a OV-1 column, and the results are shown in Fig. 1.

Optimization studies. — In each of the optimization studies, a sample of methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside (1 μmol) was dissolved in one of the solvents (100 μL) listed in Table I, and the indicated amount of ITMS was added. The mixture was maintained at the given temperature, and then iced water (300 μL) was added. When a homogeneous solution resulted, cold carbon tetrachloride (300 μL) was added, and the mixture was shaken vigorously. In each instance, the aqueous layer was washed twice with carbon tetrachloride and deionized by passing it through a column of Amberlite CG-400 (acetate form, 1 mL). The combined eluate and the water washings (30 mL) were evaporated to dryness, and the amount of D-glucose in the residue was estimated by the trimethylsilylated dithioacetal method[9]. The results are summarized in Fig. 3.

*Brominolysis and chlorinolysis of methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside.* — These reactions were performed with bromo- and chloro-trimethylsilanes in carbon tetrachloride in a manner similar to that described for iodinolysis. The chromatograms are shown in Fig. 2.

Cleavage of the interglycosidic linkages in per(trimethylsilyl)ated disaccharides. — An authentic sample of a per(trimethylsilyl)ated disaccharide (0.2 μmol) was dissolved in carbon tetrachloride (100 μL), and ITMS (20 μL) was added. The solution was kept for 30 min at 25°, and then diluted with carbon tetrachloride (300 μL). The resultant solution was cooled and shaken thrice with iced water (300 μL). The combined aqueous layers were deionized by passing them through a column of Amberlite CG-400 (acetate form, 1 mL), and the column was washed with water (30 mL). The combined eluate and washings were evaporated, and the monosaccharides in the residue were determined by the trimethylsilylated dithioacetal method[9]. The yields of monosaccharides are listed in Table II.

Cleavage of the glycosidic linkages in permethylated mono- and di-saccharides. — An authentic sample of methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranoside (0.4 μmol) or a permethylated disaccharide (0.4 μmol) was dissolved in carbon tetrachloride (100 μL), and ITMS (20 μL) was added. The solution was kept for 30 min (unless otherwise stated), and then iced water (300 μL) was added. The organic layer

was evaporated, and the remaining aqueous layer was deionized on a column of Amberlite CG-400 (acetate form, 1 mL). The combined eluate and the water washings (30 mL) were evaporated to dryness, and the partially methylated monosaccharides in the residue were analyzed by the modified dithioacetal method[10].

For comparative studies, samples of permethylated mono- and di-saccharides were hydrolyzed in 90% formic acid for 1 h at 100°, followed by 0.25M sulfuric acid for 14 h at 100°, according to the literature[11]. They were also hydrolyzed in 2M trifluoroacetic acid for 6 h at 100°. The resultant, partially methylated monosaccharides were analyzed as the dithioacetal derivatives by the same procedure. The results are summarized in Table III.

Analysis of partially methylated monosaccharides formed from permethylated oligosaccharide glycosides and polysaccharides. – Because no authentic samples of these permethylated carbohydrates were available, the parent carbohydrates were permethylated by the method of Hakomori[8], and the products were subjected, without purification, to iodinolytic cleavage. The detailed procedure was as follows. A sample of an oligosaccharide glycoside (0.4 μmol) or a polysaccharide (100 μg) was dissolved in dimethyl sulfoxide (100 μL), and a dimethyl sulfoxide solution of methylsulfinyl carbanion (50 μL) and methyl iodide (20 μL) was added. The mixture was kept overnight under nitrogen, and then water (300 μL) and chloroform (500 μL) were added. The mixture was shaken vigorously, and the chloroform layer was washed twice with water (300 μL). The chloroform layer was evaporated to dryness, and the residue was further dried under diminished pressure in a desiccator containing sodium hydroxide. The residue was treated with ITMS, and the product was hydrolyzed in the manner already described for permethylated mono- and di-saccharides. The chromatograms are shown in Fig. 4.

RESULTS AND DISCUSSION

Gas-chromatographic examination of the mixture of the per(trimethylsilyl)ethers of methyl α-D-glucopyranoside, a model carbohydrate, and ITMS indicated the presence of a major peak (peak 1) at 4.9 min, together with two minor peaks at 5.7 (peak 2) and 6.9 min (peak 3) [Fig. 1(a)]. When a mixture was treated with an excess of methanol in the presence of silver oxide and the resultant methanolyzate trimethylsilylated conventionally[7] after removal of excess methanol by evaporation, the foregoing peaks disappeared and two slower-eluting peaks emerged at 11.3 (peak 4) and 12.1 min (peak 5) [Fig. 1(b)]. These peaks were identified as those of methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α- and -β-D-glucopyranosides, respectively, by comparing their retention times with those of authentic samples. In other experiments the iodinolysis reaction-mixture was shaken with iced water. The aqueous layer was deionized with an anion-exchange resin, and the product in the deionized solution was trimethylsilylated. Analysis of the derivatized hydrolyzate revealed the presence of two peaks at 13.1 (peak 6) and 21.1 min (peak 7), assignable to the derivatives of α- and β-D-glucopyranoses, respectively [Fig. 1(c)]. Exclusive formation of anomeric

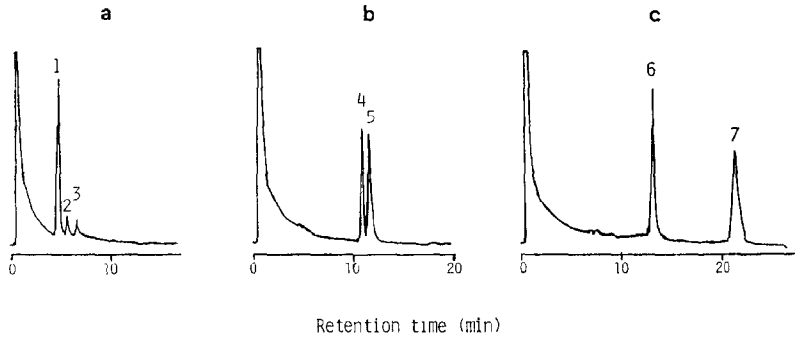


Fig. 1. Analysis of (*a*) the iodinolysis products of methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside, (*b*) methanolyzed iodinolysis products as their per(trimethylsilyl)ethers, and (*c*) hydrolyzed iodinolysis products as their per(trimethylsilyl)ethers. Peak assignments: 1–3, iodinolysis products; 4, methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside, 5, methyl 2,3,4,6-tetra-*O*-trimethylsilyl-β-D-glucopyranoside; 6, 1,2,3,4,6-penta-*O*-trimethylsilyl-α-D-glucopyranose; and 7, 1,2,3,4,6-penta-*O*-trimethylsilyl-β-D-glucopyranose.

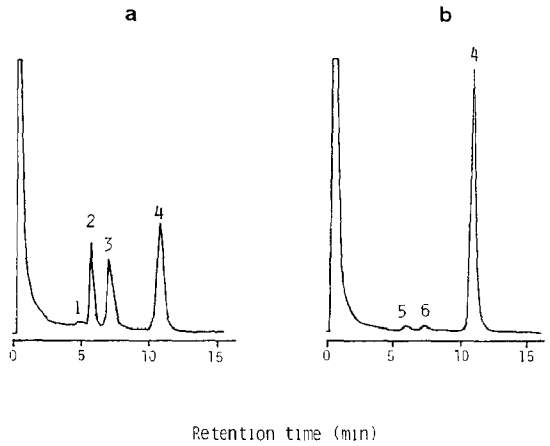


Fig. 2. Chromatograms of (*a*) the brominolysis and (*b*) chlorinolysis products of methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside. Peak assignments: 1–3, brominolysis products; 4, methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside; and 5 and 6, chlorinolysis products.

methyl glucosides and glucoses on methanolysis and hydrolysis, respectively, indicate that transformation occurred only at C-1 in this iodinolysis reaction. If any carbon atoms other than C-1 were substituted, the gas chromatograms would show additional peaks arising from such substitution-products. Although the iodinolysis products could not be isolated because they were unstable, g.l.c.–m.s. of the iodinolysis reaction-mixture suggests that the major peak (peak 1) is of per(trimethylsilyl)ated glucopyranosyl iodide, because its mass spectrum gave the molecular ion at *m/z* 578 and the relative abundance of the peak at *m/z* 217 ($Me_3SiO^2CH=^3CH\text{-}^4C^+HO\text{-}SiMe_3$) to that at *m/z* 204 ($Me_3SiO^2C^+H\text{-}^3CHOSiMe_3$ or $Me_3SiO^3C^+H\text{-}^4CHOSiMe_3$)

TABLE I

EFFECT OF REACTION SOLVENT ON THE IODINOLYSIS OF METHYL 2,3,4,6-TETRA-*O*-TRIMETHYLSILYL-α-D-GLUCOPYRANOSIDE, AS OBSERVED FROM THE YIELD OF D-GLUCOSE OBTAINED BY TREATMENT OF THE IODINOLYSIS PRODUCT WITH ICED WATER

Solvent	*Yield (%) of* D-*glucose*[a]
Carbon tetrachloride	94
Chloroform	79
Dichloromethane	78
Nitromethane	74
Acetonitrile	60
Dimethyl sulfoxide	0

[a]Reaction conditions: 30 min, 25 °, with 1.17M ITMS.

was smaller than unity (0.61), characteristic of a pyranose sugar. The spectra of the minor peaks could not be fully elucidated.

The halogenolysis reaction as mentioned for ITMS was also observed for bromotrimethylsilane. However, the yields of the brominolysis products (peaks 1–3) were low, giving an intense peak of unreacted methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside (peak 4) [Fig. 2(a)]. The yield of D-glucose in the hydrolyzate of the brominolysis product was only 9%, under the optimum conditions for iodinolysis. With the chloro analogue, the reaction was extremely slow, and the chromatogram showed almost complete recovery of the starting material [Fig. 2(b)].

Methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside was treated with

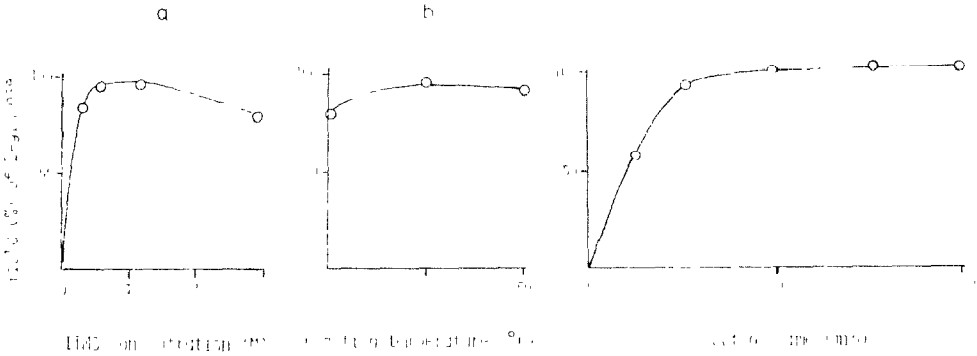


Fig. 3. (*a*) Effect of ITMS concentration on the iodinolysis of methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside in carbon tetrachloride, reaction time: 30 min, reaction temperature: 25 °; (*b*) Effect of reaction temperature on the iodinolysis of methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside in carbon tetrachloride, ITMS concentration: 1.17M, reaction time: 30 min; (*c*) Reaction course of the iodinolysis of methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside in carbon tetrachloride, ITMS concentration, 1.17M, reaction temperature: 25 °. In all of these experiments, mixtures were shaken with iced water, and the yields of D-glucose in the aqueous layers were estimated by gas chromatography as the trimethylsilylated diethyl dithioacetals.

ITMS in various solvents and the mixtures were subsequently shaken with iced water. The yields of D-glucose are compared in Table I. The results indicate that less-polar solvents give higher yields of D-glucose, and the highest yield (94%) was obtained with carbon tetrachloride. In dimethylsulfoxide, the starting material was rapidly decomposed, and as a result, no ordinary iodinolysis reaction occurred.

Fig. 3(a) shows the effect of reagent concentration on the yield of D-glucose. The yield was rapidly increased with increasing concentration to reach a maximal value at 20 μL/100 μL carbon tetrachloride, which is equivalent to 1.17M. The graph in Fig. 3(b) shows that the yield of D-glucose was relatively independent of reaction temperature in the range of 0–50°. It is also shown from Fig. 3(c) that the reaction was complete in ~30 min and the yield of D-glucose stayed constant thereafter when the reaction was conducted at 25° with 1.17M ITMS.

The foregoing results of the optimization studies indicate that the optimum ITMS concentration, reaction temperature, and reaction time for the iodinolytic cleavage of the glycosidic linkage in methyl 2,3,4,6-tetra-*O*-trimethylsilyl-α-D-glucopyranoside were 1.17M, 25°, and 30 min, respectively. Under these conditions, several disaccharides were treated with ITMS and the iodinolysis products were hydrolyzed. The cleavage rates, as obtained from the yields of monosaccharides in the hydrolyzates, are listed in Table II. It may be observed that the cleavage rate was dependent on the type of interglycosidic linkage. With β-linked glucobioses, the order of ease of cleavage was (1→4) < (1→2) < (1→3) < (1→6). The interglycosidic linkage in gentiobiose, having the β-(1→6) linkage, was quantitatively cleaved under these conditions, whereas α,α-trehalose, having the α-(1↔1) linkage, was highly resistant to ITMS. The linkage in maltose, the α-(1→4)-linked glucobiose, was more readily cleaved than that in cellobiose, its β-linked isomer. Replacement of the nonreducing D-glucosyl group in cellobiose by the D-galactosyl group, as in lactose, resulted in a slight increase of the cleavage rate.

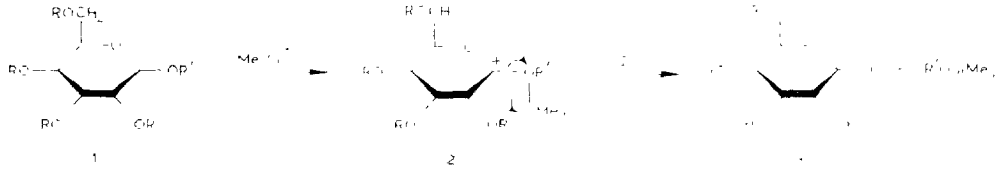
TABLE II

RATES OF CLEAVAGE OF THE INTERGLYCOSIDIC LINKAGES IN VARIOUS PER(TRIMETHYLSILYL)ATED DISACCHARIDES

Disaccharide	*Type of linkage*	*Rate (%) of cleavage*[a]
Trehalose	α,α-(1→1)	10
Sophorose	β-(1→2)	56
Laminarabiose	β-(1→3)	73
Maltose	α-(1→4)	52
Cellobiose	β-(1→4)	7
Lactose	β-(1→4)	25
Melibiose	α-(1→6)	104
Gentiobiose	β-(1→6)	100

[a]Reaction conditions: 30 min, 25°, with 1.17M ITMS.

The preferential cleavage of interglycosidic linkages attached to the primary hydroxyl groups is noteworthy, because hydrolysis with mineral acids is rather favorable for linkages attached to the secondary hydroxyl groups[13]. This reversed ease of cleavage probably arises from steric effects, as the iodinolysis reaction with ITMS is essentially considered to be SN2 substitution of the carbonium ion at C-1 of an intermediate **2** by the bulky iodide ion, with formation of the trimethylsilylated alcohol. The anomeric carbon atoms at C-1′, bound to the less-hindered oxygen atom at C-6, would be more accessible to the iodide ion than those bound to other oxygen atoms



As the SN2 reaction is highly dependent on steric factors, the protection of hydroxyl groups in methyl α-D-glucopyranoside by the less bulky methyl group would be more advantageous for cleavage of the glycosidic linkage. This expectation was realized, as iodinolysis of methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranoside afforded 2,3,4,6-tetra-*O*-methyl-D-glucose quantitatively in only 10 min. The ready scission of the glycosidic linkage in permethylated D-glucose suggested useful applications of this method to methylation analysis. From this point of view, various permethylated carbohydrates were treated with ITMS, and the iodinolysis products were treated with iced water. Fig. 4 shows some preliminary analytical results for partially methylated monosaccharides formed by these sequential reactions. The products were analyzed as their trimethylsilylated diethyl dithioacetals[10]. All of these permethylated oligosaccharides and oligosaccharide glycosides gave the partially methylated monosaccharides expected, and their molar proportions were in good agreement with theoretical values. The results obtained for permethylated polysaccharides were also consistent with those expected.

Table III gives the yields of partially methylated monosaccharides formed from some authentic permethylated disaccharides, together with the yields obtained by acid hydrolysis. The results show that the ITMS method, and also hydrolysis with trifluoroacetic acid, give almost quantitative yields of partially methylated monosaccharides for all permethylated disaccharides, whereas hydrolysis with a combination of formic acid and sulfuric acid[11] results in considerable loss of the more-volatile tetra-*O*-methylated monosaccharides in a few instances.

The results presented here indicate that iodinolytic cleavage and subsequent treatment with water may provide a novel method for hydrolyzing permethylated carbohydrates. Because of its rapidity and mildness, it may prove of value in methylation analysis.

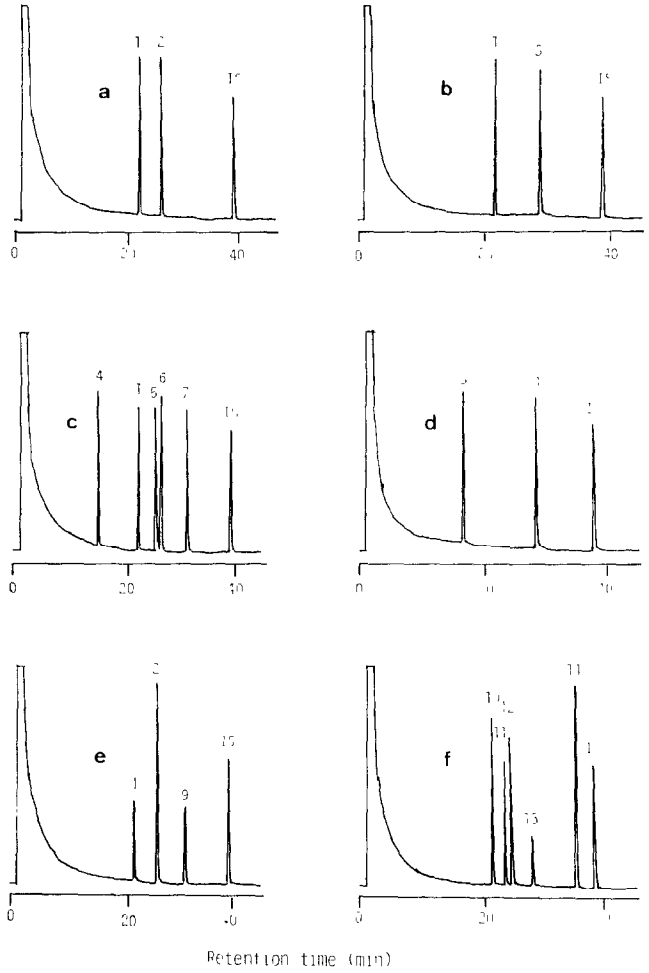


Fig. 4. Analysis of the partially methylated monosaccharides, formed by the reaction of various permethylated carbohydrates with ITMS, followed by treatment of the products with iced water. The monosaccharide derivatives were analyzed as trimethylsilylated dicthyl dithioacetals by the modified dithioacetal method[10]. Peak assignments: 1, 2,3,4,6-tetra-*O*-methyl-D-glucose; 2, 2,3,6-tri-*O*-methyl-D-glucose; 3, 2,3,4-tri-*O*-methyl-D-glucose; 4, 2,3,4-tri-*O*-methyl-D-xylose; 5, 2,3,6-tri-*O*-methyl-D-galactose; 6, 2,4,6-tri-*O*-methyl-D-galactose; 7, 4,6-di-*O*-methyl-D-glucose; 8, 2,3,4-tri-*O*-methyl-L-rhamnose; 9, 2,3-di-*O*-methyl-D-glucose; 10, 2,3,4,6-tetra-*O*-methyl-D-mannose; 11, 3,4,6-tri-*O*-methyl-D-mannose; 12, 2,4,6-tri-*O*-methyl-D-mannose; 13, 2,3,4-tri-*O*-methyl-D-mannose; 14, 3,4-di-*O*-methyl-D-mannose; IS (internal standard), 3-*O*-methyl-D-glucose. Samples (molar proportions): (*a*) maltose (peak 1:peak 2 = 1:1.05); (*b*) gentiobiose (peak 1:peak 3 = 1:0.96); (*c*) digitonin (peak 4:peak 1:peak 5:peak 6:peak 7 = 1.10:1:1.00:1.08:1.14); (*d*) naringin (peak 8:peak 3 = 1:1.02); (*e*) rabbit-liver glycogen (peak 1:peak 2:peak 9 = 1:11.9:1.47); and (*f*) yeast mannan (peak 10:peak 11:peak 12:peak 13:peak 14 = 1:0.62:0.91:0.26:2.14).

TABLE III

YIELDS OF PARTIALLY METHYLATED MONOSACCHARIDES FORMED FROM SOME PERMETHYLATED DISACCHARIDES

Permethylated disaccharide	*Partially methylated monosaccharide(s) formed*	*Yield (%)*		
		ITMS method[a]	*Hydrolysis with formic acid–sulfuric acid*[b]	*with trifluoroacetic acid*[c]
2,3,4,6,2′,3′,4′,6′-Octa-*O*-methyl-α,α-trehalose	2,3,4,6-tetra-*O*-methyl-D-glucose	96	95	94
1,2,3,6,2′,3′,4′,6′-Octa-*O*-methylmaltose	2,3,6-tri-*O*-methyl-D-glucose	99	95	107
	2,3,4,6-tetra-*O*-methyl-D-glucose	106	62	86
1,2,3,6,2′,3′,4′,6′-Octa-*O*-methyllactose	2,3,6-tri-*O*-methyl-D-glucose	110	116	118
	2,3,4,6-tetra-*O*-methyl-D-galactose	109	83	102
1,2,3,4,2′,3′,4′,6′-Octa-*O*-methylgentiobiose	2,3,4-tri-*O*-methyl-D-glucose	86	94	87
	2,3,4,6-tetra-*O*-methyl-D-glucose	98	58	96

[a]Reaction with 1.17M ITMS for 30 min at 25°, followed by treatment with iced water. [b]Heating in 90% formic acid for 1 h at 100°, followed by 0.25M sulfuric acid for 14 h at 100°. [c]Heating in 2M trifluoroacetic acid for 6 h at 100°.

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