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DEAMINATION OF 2-AMINO-2-DEOXYHEXITOLS AND OF THEIR PER-*O*-METHYLATED DERIVATIVES WITH NITROUS ACID*

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ABSTRACT

The products of nitrous acid deamination of per-*O*-methylated 2-amino-2-deoxy-D-glucitol and of 2-amino-2-deoxy-3-*O*-β-D-galactopyranosyl-D-glucitol and its per-*O*-methylated derivative have been characterized by g.l.c.–mass spectrometry after treatment with sodium borodeuteride and further substitution by acetylation, methylation, or (trideuteriomethyl)ation. The results confirm that the most important reaction pathway (*1*) involves a 1→2-hydride shift to give 2-deoxy-D-*arabino*-hexoses, but that significant side-reactions include (*2*) solvolytic displacement at C-2, (*3*) a 3→2-hydride shift, to give 2-deoxy-D-*erythro*-3-hexuloses, and (*4*) a C-4→C-2 migration to give 2-deoxy-2-*C*-(hydroxymethyl)-D-ribose and -D-arabinose. Reactions (*3*) and (*4*) result in elimination of the original 3-*O*-substituents, with the exposure of new reducing groups, from oligosaccharides terminated by 3-*O*-substituted 2-amino-2-deoxyhexitols.

INTRODUCTION

Kochetkov *et al.*[2] have shown that 2-deoxyhexose-terminated oligosaccharides are formed on nitrous acid deamination of the corresponding oligosaccharides terminated by aminohexitol residues. Although 2-deoxy-D-*arabino*-hexose is the single most abundant product from the deamination of 2-amino-2-deoxy-D-glucitol, Bando and Matsushima[3] found that its formation is accompanied by that of smaller proportions of 2-deoxy-2-*C*-(hydroxymethyl)-D-ribose and -D-arabinose, 2-deoxy-D-*erythro*-3-hexulose, and D-mannitol. The multiplicity of alternative reaction-pathways in the deamination of substituted aminohexitols was further suggested by the results of studies in this laboratory on the deamination of 2-amino-2-deoxy-D-galactitol-terminated, oligosaccharide alditols formed, by reductive elimination followed by *N*-deacetylation, from *O*-glycosyl-substituted L-serine or L-threonine units in hog-gastric mucin (unpublished results). Analysis of the products showed that deamination

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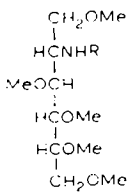
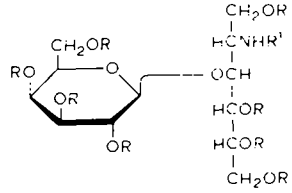
resulted in the exposure of new reducing groups, other than those of 2,5-anhydrohexoses, from the cleavage of 2-amino-2-deoxyglycosidic linkages and of 2-deoxyhexose from the 2-amino-2-deoxy-D-galactitol termini. A large number of oligosaccharide units from hog-gastric mucin have been individually characterized by Kochetkov *et al.*[4,5] and have been shown to contain 4-*O*-substituted, but not 3-*O*-substituted, 2-amino-2-deoxy-D-glucose residues. New reducing groups could not, therefore, arise through the alternative ring-contraction that accompanies formation of 2,5-anhydrohexose in the deamination of 3-*O*-substituted 2-amino-2-deoxyglycosides[1,6]. In order to account for the exposure of such reducing groups during the deamination, we have examined the products from the treatment of per-*O*-methylated 2-amino-2-deoxy-D-glucitol, and of 2-amino-2-deoxy-3-*O*-β-D-galactopyranosyl-D-glucitol and its per-*O*-methylated derivative.

RESULTS AND DISCUSSION

2-Acetamido-2-deoxy-D-glucitol was methylated with dimethyl sulfate and sodium hydroxide, to give a per-*O*-methylated derivative (**1**), with no significant accompanying *N*-methylation. Hydrazinolysis furnished the parent amine (**2**), which was treated with nitrous acid; the deamination products were treated with sodium borodeuteride, and the reduction products acetylated. The resulting, partially methylated alditol acetates were examined by g.l.c.–mass spectrometry (m.s.), and evidence was obtained for the formation of the following eight compounds in the relative proportions shown. 2,5-Anhydro-1,3,4,6-tetra-*O*-methyl-D-mannitol (**3**, 2.4%) was identical with a synthetic sample. The second and third compounds were characterized as a 3-*O*-acetyl-2-deoxy-1,4,5,6-tetra-*O*-methylhexitol-*3-d* (**4**, 8.6%) and a branched-chain 1-*O*-acetyl-2-deoxy-2-(methoxymethyl)-3,4,5-tri-*O*-methylpentitol-*1-d* (**6**, 10.9%). The presence of a very intense, fragment ion at *m/e* 144 in the mass spectrum

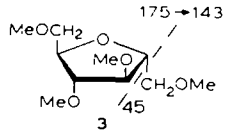


1 R = Ac
2 R = H



11 R = H, R' = Ac
12 R = H, R' = H
13 R = Me, R = Ac
14 R = Me, R' = H

of **6**, its almost complete absence from that of **4**, and the appearance of a relatively intense fragment-ion at *m/e* 128 from compound **4** served to differentiate these constitutional isomers. The next two compounds were insufficiently separated to permit obtaining their individual mass spectra, but the observed fragment-ions pointed to the presence of a second 3-*O*-acetyl-2-deoxy-1,4,5,6-tetra-*O*-methylhexitol-*3-d*



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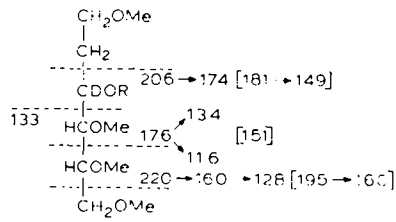
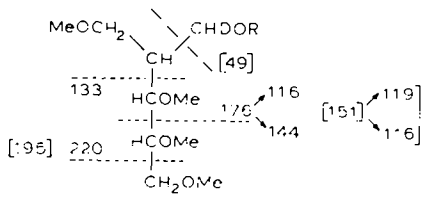
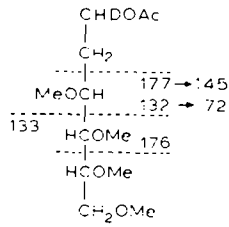


4 and **5**, R = Ac
19 and **20**, R = CD_3*



6 and **7**, R = Ac
21 and **22**, R = CD_3*



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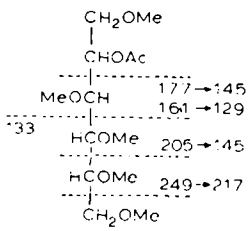
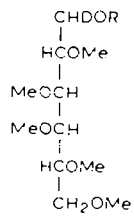


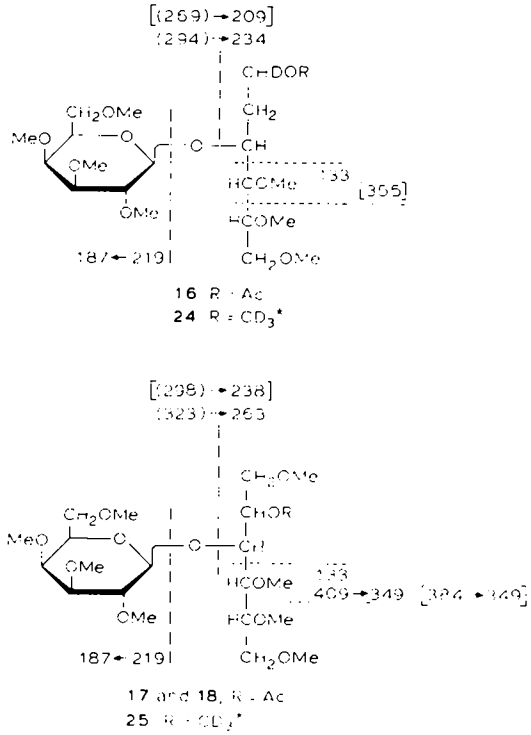
9 and **10**



15 R = Ac
23 R = CD_3

(**5**, 8.6%) and a second, branched-chain 1-*O*-acetyl-2-deoxy-2-(methoxymethyl)-3,4,5-tri-*O*-methylpentitol-*1-d* (**7**, 8.6%). It was not possible to assign individual configurations to the two pairs of diastereomers (**4** and **5**, and **6** and **7**). The single, most-abundant product was likewise characterized as 1-*O*-acetyl-2-deoxy-3,4,5,6-tetra-*O*-methyl-D-*arabino*-hexitol-*1-d* (**8**, 44.4%) from its mass spectrum, with the configuration assigned on the basis of its probable mode of formation. The 2-*O*-acetyl-1,3,4,5,6-penta-*O*-methylhexitols (**9** and **10**, 5.4 and 11.1%), which contained no deuterium, were probably the D-*gluco* and D-*manno* epimers, the former being chromatographically indistinguishable from a synthetic sample of the D-*gluco* derivative.

The formation of these various products confirms the results of Bando and Matsushima[3] concerning the complexity of the reaction of 2-amino-2-deoxy-D-glucitol with nitrous acid. The competing reactions are best rationalized[7] as involving (*1*) a 1→2-hydride shift, to give a 2-deoxy-D-*arabino*-hexose, (*2*) solvolytic displacement at C-2, (*3*) a 3→2-hydride shift, to give a 2-deoxy-D-*erythro*-3-hexulose, (*4*) a



C-4→C-2 migration, to give the epimeric 2-deoxy-2-*C*-(hydroxymethyl)-D-ribose and -D-arabinose, and (*5*) intramolecular displacement leading to 2,5-anhydrohexose formation. Reaction (*4*) may proceed stereospecifically, but, as in the formation of branched glycosides[6], epimerization may occur during the reaction, or during subsequent treatment with sodium borohydride. The formation of 2,5-anhydro-D-mannitol as a minor product in the deamination of 2-amino-2-deoxy-D-glucitol was suspected, but not directly proved, by Bando and Matsushima[3].

2-Acetamido-2-deoxy-3-*O*-β-D-galactopyranosyl-D-glucitol[8] (**11**) was *N*-deacetylated to give the amine **12**, which was deaminated with nitrous acid, and the products were treated with sodium borodeuteride. A portion of the reaction mixture was acetylated, and g.l.c. examination showed the presence, *inter alia*, of the peracetates of 2-deoxy-D-*arabino*- and -D-*ribo*-hexitols and galactitol. The major portion of the reaction mixture was methylated by the Hakomori procedure[9], and examination of the products by g.l.c.–m.s. showed the presence of per-*O*-methylated derivatives of four deoxyhexitols (probably two linear 2-deoxyhexitols and two branched alditols, but only one of each type was characterized with reasonable certainty), galactitol, and a 2-deoxy-3-*O*-hexopyranosylhexitol, all with deuterium incorporation, and a 3-*O*-hexopyranosylhexitol without incorporation of deuterium, for which no separation of C-2 epimers was achieved. More-detailed information was obtained by a study of the deamination of amine **14**, formed from the per-*O*-methylated disaccharide

alditol (**13**), followed by treatment of the products with sodium borodeuteride. A portion of the products was acetylated, and examination of the products by g.l.c.–m.s. established the presence of those compounds (**4**–**7**) formed from per-*O*-methylated 2-amino-2-deoxy-D-glucitol by reaction pathways (*3*) and (*4*), together with 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-D-galactitol-*1-d* (**15**). Three disaccharide alditol derivatives were detected by using a different g.l.c. column (Superpak 20M), and their mass spectra were consistent with their formulation as the 1-*O*-acetyl-2-deoxyhexitol-*1-d* derivative (**16**) and an epimeric pair of 2-*O*-acetylhexitol derivatives (**17** and **18**). Another portion of the reaction mixture was further alkylated with trideuteriomethyl iodide and both monosaccharide (**19**–**23**) and disaccharide (**24** and **25**) alditols were characterized by g.l.c.–m.s. Of the epimeric pairs of 2-deoxyhexitols-*1-d* (**19** and **20**) and branched-chain alditols (**21** and **22**), only one compound from each pair was sufficiently separated to give mass spectra that could be interpreted unambiguously, but the presence of the second member of each stereoisomeric pair as the preponderant component of other g.l.c. fractions was clearly indicated by the presence of fragment ions at *m/e* 49 of low and high intensity, respectively, relative to those at *m/e* 45. The mass spectra of the two per-*O*-methylated disaccharide alditol fractions (**24** and **25**) served to establish their substitution patterns. The conditions of separation did not permit the resolution of the disaccharide alditol fraction (**25**), although both C-2 epimers were presumably formed.

In relation to the use of nitrous acid deamination in the structural characterization of complex amino-oligosaccharide alditols of the type liberated by reductive elimination from *O*-glycosylic linkages to L-serine or L-threonine units in mucin-type glycoproteins[10], the compounds that have been recognized as deamination products from the per-*O*-methylated aminodisaccharide alditol **14** are of significance in two respects. Firstly, deamination followed by treatment with sodium borodeuteride furnishes oligosaccharide alditols in which (*a*) deuterium-labelled 2-deoxyhexitol (reaction pathway *1*) and (*b*) unlabelled hexitol (pathway *2*) units originate from terminal 2-amino-2-deoxyhexitol residues in the parent oligosaccharide chains. Secondly, reducing groups liberated and then labelled on treatment with sodium borodeuteride are now recognized as arising from the loss of 3-*O*-substituents from either 2-amino-2-deoxyhexitol termini or, as previously shown[1], from the alternative ring-contraction that accompanies 2,5-anhydrohexose formation on deamination of equatorially oriented 2-amino-2-deoxyglycosides. However, in the former instance, there will be accompanying formation of deuterium-labelled 2-deoxyhexitols or branched-chain alditols. Although 2,5-anhydrohexitol derivatives are formed as minor products from the deamination of 2-amino-2-deoxyhexitols, they are formed directly, and treatment with sodium borodeuteride does not result in deuterium labelling; they are thus readily distinguished from the products of deamination of 2-amino-2-deoxyglucosidic linkages.

EXPERIMENTAL

General methods. — Evaporations were conducted under diminished pressure

at bath temperatures of 40° or lower. Optical rotations were measured with a Perkin–Elmer model 141 polarimeter at 20 ±2°. N.m.r. spectra were recorded at 60 MHz with a Varian EM-360 spectrometer for solutions in chloroform-*d* containing 1% of tetramethylsilane as the internal standard, unless stated otherwise.

G.l.c. was performed, at temperatures indicated, with Perkin–Elmer 990 and Tracor 560 chromatographs, using columns of Gas Chrom Q coated with (*A*) 3% of silicone-polyester copolymer ECNSS-M, and (*B*) 3% of silicone gum OV-225; (*C*) an OV-225 S.C.O.T. column; and (*D*) a column of Superpak 20M (Analab). For g.l.c.–m.s., columns were attached *via* a Watson–Biemann separator to a Perkin–Elmer–Hitachi RMU-6 mass spectrometer, operated with an inlet temperature of 250°, an ionization potential of 70 eV, and an ion-source temperature of ~250°.

2-Acetamido-2-deoxy-1,3,4,5,6-penta-O-*methyl*-D-*glucitol* (**1**). — 2-Acetamido-2-deoxy-D-glucose was reduced with sodium borohydride in water for 18 h. The excess of hydride was decomposed, sodium ions were removed by treatment with Amberlite IR-120 (H^+) resin, the suspension was filtered, and the filtrate was evaporated four times with methanolic, 2% acetic acid to remove boric acid as methyl borate. The resulting, syrupy alditol was per-*O*-methylated with dimethyl sulfate and 30% aqueous sodium hydroxide, and continuous extraction of the reaction mixture with dichloromethane furnished the methylated alditol (**1**) as a syrup that had $[\alpha]_D$ +19.8° (*c* 1.4, chloroform) and gave a single peak in g.l.c. on column *B* at 170°, *T* (relative to 2,3,4,6-tetra-*O*-methyl-D-glucitol diacetate as unity) 0.88; n.m.r. data: δ 2.20 (s, 3 H, NAc), 3.20–4.30 (broad m, 23 H, H-1,2,3,4,5,6 and OCH_3), and 6.30 (d, 1 H, NH); *m/e* 248 (48), 216 (77), 204 (89), 177 (30), 160 (89), 133 (53), 116 (90), and 45 (100).

N-*Deacetylation–deamination of* **1**. — Methylated alditol **1** (100 mg) in hydrazine (10 mL) containing hydrazine sulfate (100 mg) was boiled for 2 days under reflux. Hydrazine was removed by co-distillation with toluene under diminished pressure. The residue was dissolved in water (5 mL) containing sodium nitrite (300 mg), and M sulfuric acid was added dropwise, with cooling, to bring the pH of the solution to 4. The solution was kept for 1 h at room temperature, and extracted with dichloromethane (5 × 5 mL), and the extracts were combined, dried, and evaporated; the residue was reduced with sodium borodeuteride, and the product acetylated with acetic anhydride and pyridine as usual. The acetylation products were examined by g.l.c.–m.s., using column *B* at 130°, and found to include the following fractions (in the proportions given in parentheses) having retention times (*T*, relative to that of methyl 2,3,4,6-tetra-*O*-methyl-β-D-glucopyranoside as unity), and to contain compounds of the assigned structures: (*i*) **3** (2.4%), *T* 1.06, *m/e* 220 (M^+, 0.5), 188 (6), 175 (37), 156 (36), 143 (67), and 45 (100), indistinguishable from a synthetic sample of 2,5-anhydro-1,3,4,6-tetra-*O*-methyl-D-mannitol; (*ii*) **4** (8.6%), *T* 2.22, *m/e* 220 (2.5), 206 (1.3), 176 (97), 174 (5), 160 (25), 134 (22), 133 (15), 128 (25), 116 (48), 89 (43), and 45 (100); (*iii*) **6** (10.9%), *T* 2.53, *m/e* 220 (4.8), 176 (70), 144 (78), 133 (8), 116 (99), 89 (31), and 45 (100); (*iv*) **5** (8.6%), *T* 2.88, *m/e* 220 (10), 206 (1.5), 176 (29), 144 (35), 133 (12), 116 (85), 89 (32), and 45 (100); (*v*) **7** (8.6%),

T 2.94, *m/e* 220 (8.2), 206 (1.1), 176 (80), 160 (18), 134 (18), 133 (12), 128 (23), 116 (65), 89 (33), and 45 (100); (*vi*) **8** (44.4%), *T* 3.38, *m/e* 188 (1), 177 (0.3), 176 (1), 145 (2.5), 133 (20), 132 (62), 89 (23), 72 (100), and 45 (86); (*vii*) **9** (5.4%), *T* 4.06, (*m/e* 249 (1), 205 (20), 177 (2), 161 (40), 145 (51), 133 (20), 129 (51), 117 (10), 89 (20), and 45 (100), indistinguishable from a sample of 2-*O*-acetyl-1,3,4,5,6-penta-*O*-methyl-D-glucitol formed from permethylated sophorobiitol by hydrolysis and acetylation; and (*viii*) **10** (11.1%), *T* 4.75, whose mass spectrum was identical to that of compound **9**.

N-*Deacetylation–deamination of 2-acetamido-2-deoxy-3*-O-β-D-*galactopyranosyl*-D-*glucitol* (**11**). — Compound[8] **11** (25 mg) in hydrazine (4 mL) containing hydrazine sulfate (40 mg) was boiled under reflux for 2 days and the hydrazine was removed by co-distillation with toluene under diminished pressure. The residue was dissolved in water (2 mL) containing sodium nitrite (400 mg), M sulfuric acid was added dropwise, with cooling, to bring the pH of the solution to 3.5, and the solution was kept for 1 h at room temperature. Urea was added to decompose the excess of nitrous acid, the pH of the solution was brought to 7 by the addition of sodium hydrogencarbonate, sodium borodeuteride (50 mg) was added, and the solution was kept overnight. Dowex 50 (H^+) resin was added to decompose the excess of hydride and to render the solution neutral, the suspension was filtered, and the filtrate evaporated. A portion of the residue was treated with acetic anhydride–pyridine, and g.l.c. of the resulting alditol acetates on column *B* at 200° revealed, *inter alia*, compounds having the retention times of the peracetates of 2-deoxy-D-*ribo*- and -D-*arabino*-hexitols and galactitol.

The major portion of the aforementioned residue was methylated by the Hakomori procedure[9], to give a mixture of per-*O*-methylated alditols and disaccharide alditols which was examined by g.l.c.–m.s. (column *C*; 100°, 6°/min to 210° and hold). The following seven fractions were recognized, and structural assignments, where made, are on the basis of the fragment-ions mentioned: (*1*) 2-deoxypenta-*O*-methylhexitol-*3-d*, *T* (relative to hexa-*O*-methylgalactitol as unity) 0.73 (eluted at 172.2°), *m/e* 192 (3.5), 178 (5), 160 (2), 148 (9), 133 (5), 104 (16), 101 (29), 89 (16), 72 (9), and 45 (100); (*2*) linear or branched deoxyhexitol-*d* pentamethyl ether, *T* 0.74 (eluted at 173.8°); (*3*) 2-deoxy-2-(methoxymethyl)-tetra-*O*-methylpentitol-*1-d*, *T* 0.80 (eluted at 179.8°), *m/e* 148 (15), 133 (6), 116 (28), 104 (60), 101 (85), 89 (23), 46 (100), and 45 (96); (*4*) linear or branched deoxyhexitol-*d* pentamethyl ether, *T* 0.87 (eluted at 186.4°); (*5*) hexa-*O*-methylgalactitol-*1-d*, *T* 1.00 (eluted at 199°), mass spectrum identical with that of a synthetic sample; (*6*) 2-deoxy-1,4,5,6-tetra-*O*-methyl-3-*O*-(2,3,4,6-tetra-*O*-methylhexopyranosyl)-hexitol-*1-d*, *T* 2.89 (eluted at 210°), *m/e* 266 (45, abJ_1), 219 (69, aA_1), 206, 89 bA_1), 187 (84, aA_2), 133 (21), 89 (100), 46 (83), and 45 (92); (*7*) 1,2,4,5,6-penta-*O*-methyl-3-*O*-(2,3,4,6-tetra-*O*-methylhexopyranosyl)hexitol, *T* 3.46 (eluted at 210°), *m/e* 295 (8, abJ_1), 235 (26, bA_1), 219 (11, aA_1), 187 (33, aA_2), 133 (98), 101 (100), 89 (46), and 45 (98).

Per-O-*methylation of 2-acetamido-2-deoxy-3*-O-β-D-*galactopyranosyl*-D-*glucitol* (**11**), *followed by* N-*deacetylation–deamination of* **13**. — The disaccharide alditol[8] **11**

(80 mg) was per-*O*-methylated with dimethyl sulfate and 30% aqueous sodium hydroxide, to give the methylated disaccharide alditol (**13**) as a syrup (52 mg); *m/e* 497 (M^+, 0.2), 452 (5, M − CH_2OCH_3), 408 (18, M − 89), 364 (29, M − 133), 322 (8, abJ_1), 262 (42, bA_1), 219 (21, aA_1), 187 (87, aA_2), 133 (36), 89 (65), and 45 (100).

The per-*O*-methylated disaccharide alditol **13** (11 mg) was successively *N*-deacetylated, deaminated, and reduced with sodium borodeuteride, as described for compound **1**. A portion of the reaction products was further alkylated with trideuteriomethyl iodide and sodium hydride in dimethyl sulfoxide[9], to give a mixture of per-*O*-methylated alditols and disaccharide alditols which was examined by g.l.c.–m.s. (column *C*; 130°, 4°/min to 210° and hold). The following seven fractions were observed, and structural assignments, where made, are on the basis of the fragment-ions mentioned: (*1*) linear or branched deoxyhexitol-*d* pentamethyl ether, *T* 0.52 (eluted at 149.6°); (*2*) **21**, 0.55 (eluted at 150.7°), *m/e* 195 (32), 151 (68), 133 (9), 119 (23), 116 (46), 89 (39), 72 (100), 49 (69), and 45 (82); (*3*) linear or branched deoxyhexitol-*d* pentamethyl ether, *T* 0.63 (eluted at 153.8°); (*4*) **19**, *T* 0.88 (eluted at 163.2°), *m/e* 195 (2), 181 (4), 151 (58), 149 (11), 133 (5), 89 (23), and 45 (100); (*5*) 2,3,4,6-tetra-*O*-methyl-1,5-di-*O*-($^2H_3$-methyl)galactitol-*1-d* (**23**), *T* 1.00 (eluted at 167.5°), mass spectrum identical with that of a synthetic sample; (*6*) **24**, *T* 2.90 (eluted at 210°), *m/e* 355 (2, M − 89), 269 (5.5, abJ_1), 219 (20, aA_1), 209 (40, bA_1), 187 (46, aA_2), 133 (15), 101 (100), 89 (70), and 45 (86); (*7*) **25**, *T* 3.46 (eluted at 210°), *m/e* 384 (1, M − 89), 298 (6, abJ_1), 238 (24, bA_1), 219 (12, aA_1), 187 (38, aA_2), 133 (8), 89 (25), 88 (100), and 45 (65).

A second portion of the reaction products from the deamination of the per-*O*-methylated disaccharide alditol **13** was acetylated with acetic anhydride–pyridine, and the resulting acetates were examined by g.l.c.–m.s. in column *C* at 140°, for analysis of partially methylated alditol acetates. The following four fractions were observed: (*1*) **4**, *T* (relative to 2,3,4,6-tetra-*O*-methylgalactitol 1,5-diacetate as unity) 0.46, *m/e* 265 (1.5, M^+), 220 (1.3), 206 (1), 176 (5), 160 (12), 134 (12, 133) (7), 128 (12), 116 (13), 89 (21), and 45 (100); (*2*) **6**, *T* 0.51 *m/e* 265 (1, M^+), 220 (2), 176 (37), 144 (49), 133 (3), 116 (77), 89 (25), and 45 (100); (*3*) probably a mixture of **5** and **7**, *T* 0.54, *m/e* 265 (1.3, M^+), 220 (4), 176 (49), 160 (11), 144 (12), 134 (13), 133 (9), 128 (14), 116 (23), 89 (18), and 45 (100); and (*4*) 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methylgalactitol-*1-d* (**15**), *T* 1.00, mass spectrum identical with that of a synthetic sample. The same mixture was examined by g.l.c.–m.s. on column *D* at 200° for analysis of the disaccharide alditol components, and the following three fractions were observed: (*i*) **16**, *m/e* 294 (8, abJ_1), 234 (79, bA_1), 219 (16, aA_1), 187 (53, aA_2), 133 (19), 89 (88), 88 (100), and 45 (88); (*ii*) and (*iii*) **17** and **18**, with essentially similar mass spectra having prominent fragment-ions at *m/e* 409 (2, M − 89), 349 (1, M − 89 − CH_3CO_2H), 323 (5, abJ_1), 263 (17, bA_1), 219 (6, aA_1), 187 (25, aA_2), 133 (3.5), 89 (42), and 45 (100).

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