ELSEVIER

Carbohydrate Research 299 (1997) 143–149

CARBOHYDRATE RESEARCH

Authentic standards for the reductive-cleavage method. The positional isomers of partially methylated and acetylated or benzoylated 1,5-anhydro-D-xylitol

Larry E. Elvebak II [a], Vippra Knowles [b], Gary R. Gray [b,*]

[a] *Hercules, Inc., Research Center, Wilmington, DE 19808, USA*
[b] *The Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA*

Received 22 August 1996; accepted 17 December 1996

Abstract

Described herein is the synthesis of the eight positional isomers of methylated and acetylated or benzoylated 1,5-anhydro-D-xylitol. The compounds are generated simultaneously from 1,5-anhydro-D-xylitol by sequential partial methylation and benzoylation. The individual isomers are obtained in pure form by high-performance liquid chromatography. Debenzoylation and acetylation yielded the desired acetates. Reported herein are the ^{1}H NMR spectra of the benzoates and the electron-ionization mass spectra of the acetates and the tri-*O*-methyl derivative. Also reported for the acetates and the tri-*O*-methyl derivative are their linear temperature-programmed gas–liquid chromatography retention indices on three different capillary columns. © 1997 Elsevier Science Ltd.

Keywords: Reductive-cleavage; D-Xylitol; 1,5-Anhydro-, partially methylated and acylated

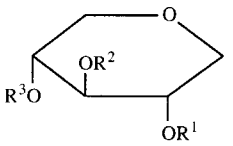
1. Introduction

We recently described a general procedure for the synthesis of authentic standards for the reductive-cleavage method [1–3] for glycosyl-linkage analysis as illustrated by the synthesis of the eight positional isomers of methylated and acetylated or benzoylated 1,5-anhydro-D-fucitol [4]. Described herein is the application of this approach to the synthesis of authentic standards derivable from D-xylopyranosyl residues, namely the positional isomers of methylated and acetylated or benzoylated 1,5-anhydro-D-xylitol **1–8**. As an aid to those who wish to use the reductive-cleavage method, ^{1}H NMR spectra of the five methylated and benzoylated positional isomers of 1,5-anhydro-D-xylitol **2b–8b** are reported, as are the electron-ionization (EI) mass spectra of the corresponding acetates **2a–8a** and the tri-*O*-methyl derivative **1**. In addition, the retention data of the acetates **2a–8a** and the tri-*O*-methyl derivative **1** on three different GLC columns are reported as linear temperature programmed gas–liquid chromatography retention indices (LTPGLCRI), a particularly accurate method of identification, but one not used until re-

* Corresponding author.

0008-6215/97/$17.00 © 1997 Elsevier Science Ltd. All rights reserved.
PII S0008-6215(97)00009-8

cently [4] for carbohydrate derivatives useful in glycosyl-linkage analysis.



	R^1	R^2	R^3
1	Me	Me	Me
2a	Ac	Me	Me
2b	Bz	Me	Me
3a	Me	Ac	Me
3b	Me	Bz	Me
4a	Me	Me	Ac
4b	Me	Me	Bz
5a	Ac	Ac	Me
5b	Bz	Bz	Me
6a	Ac	Me	Ac
6b	Bz	Me	Bz
7a	Me	Ac	Ac
7b	Me	Bz	Bz
8a	Ac	Ac	Ac
8b	Bz	Bz	Bz

2. Results

Synthesis.—The tri-*O*-methyl **1**, tri-*O*-acetyl **8a**, and tri-*O*-benzoyl **8b** derivatives of 1,5-anhydro-D-xylitol were prepared from the latter by total methylation [5], acetylation, and benzoylation, respectively.

Table 1
Reversed-phase HPLC capacity factors (k') of compounds **2b–8b** [a]

Compound [b] (position of benzoyl)	k' [c]
3b (3-)	1.92
2b, 4b (2-, and 4-)	2.31
5b, 7b (2,3-, and 3,4-)	4.03
6b (2,4-)	4.19
8b (2,3,4-)	4.98

[a] Capacity factors (k') were calculated from the equation $k'(x) = (t_{r(x)} - t_m)/t_m$ where $k'(x)$ is the capacity factor of the compound of interest (x), $t_{r(x)}$ the absolute retention time of the compound of interest (x), and t_m is the dead time. Dead time was estimated from the equation $t_m = (0.5 \cdot L \cdot d_c^2)/F$ where 0.5 is a unitless constant, L is the length of the column in centimeters, d_c is the column diameter in centimeters, and F is the column flow rate in mL/min [7].
[b] Compounds listed in the order in which they eluted from the C_{18} column.
[c] Reversed-phase HPLC was conducted using a 5-μm particle-size Rainin Dynamax Microsorb semipreparative C_{18} column.

The remaining four partially methylated and benzoylated positional isomers **2b–7b** were prepared by partial methylation [6] of 1,5-anhydro-D-xylitol, followed by benzoylation in situ [4]. The resultant mixture of partially methylated 1,5-anhydro-D-xylitol benzoates was then separated by semipreparative reversed-phase HPLC using a Rainin C_{18} column (Table 1). The individual components were isolated and, after removal of solvent, were identified by ^{1}H NMR

Table 2
^{1}H NMR data (δ in ppm, J in Hz in parentheses) of partially methylated 1,5-anhydro-D-xylitol benzoates **2b–8b** [a,b]

Compound (position of benzoyl)	H-1e	H-1a	H-2 [c]	H-3 [c]	H-4 [c]	H-5e	H-5a	O–Me
2b, 4b	4.10 dd	3.33–3.39	5.05 dt	3.46 t	3.33–3.39	4.03 dd	3.30 dd	3.51,3.58
(2- and 4-)	(4.9, 11.4)	complex	(4.9, 8.2)	(7.6)	complex	(4.0, 11.0)	(8.7, 11.0)	
3b	4.80 dd	3.32 dd	3.44 dt	5.28 t	3.44 dt	4.80 dd	3.32 dd	3.39 [d]
(3-)	(4.8, 11.4)	(9.5, 11.4)	(4.8, 9.0)	(8.4)	(4.8, 9.0)	(4.8, 11.4)	(9.5, 11.4)	
5b, 7b	4.25 dd	3.46 dd [e]	5.22 dt	5.57 t	3.60 dt	4.19 dd	3.41 dd	3.45
(2,3- and 3,4-)	(5.0, 11.3)	(9.5, 11.3)	(5.0, 9.2)	(8.7)	(4.9, 8.9)	(4.9, 11.6)	(9.5, 11.6)	
6b	4.06 dd	3.84 dd	5.10 br q [f]	3.79 t	5.10 br q [f]	4.06 dd	3.84 dd	3.61
(2,4-)	(3.0, 12.5)	(4.5, 12.5)	(4.0)	(4.7)	(4.0)	(3.0, 12.5)	(4.5, 12.5)	
8b	4.31 dd	3.66 dd	5.34 dt	5.83 t	5.34 dt	4.31 dd	3.66 dd	
(2,3,4-)	(4.7, 11.6)	(8.3, 11.6)	(4.7, 8.1)	(8.1)	(4.7, 8.1)	(4.7, 11.6)	(8.3, 11.6)	

[a] Additional resonances were observed for benzoyl hydrogens at δ 7.33–8.11.
[b] Multiplicities include br, broad; dd, doublet of doublets; t, triplet; dt, doublet of triplets; q, quartet; m, multiplet.
[c] The resonances assigned as a triplet (t) and a doublet of triplets (dt) were actually a doublet of doublets (dd) and doublet of doublets of doublets (ddd), respectively, with a pair of coupling constants having nearly equal magnitude.
[d] Singlet integrates to six hydrogens.
[e] Resonance partially obscured.
[f] Resonance is observed as an apparent quartet.

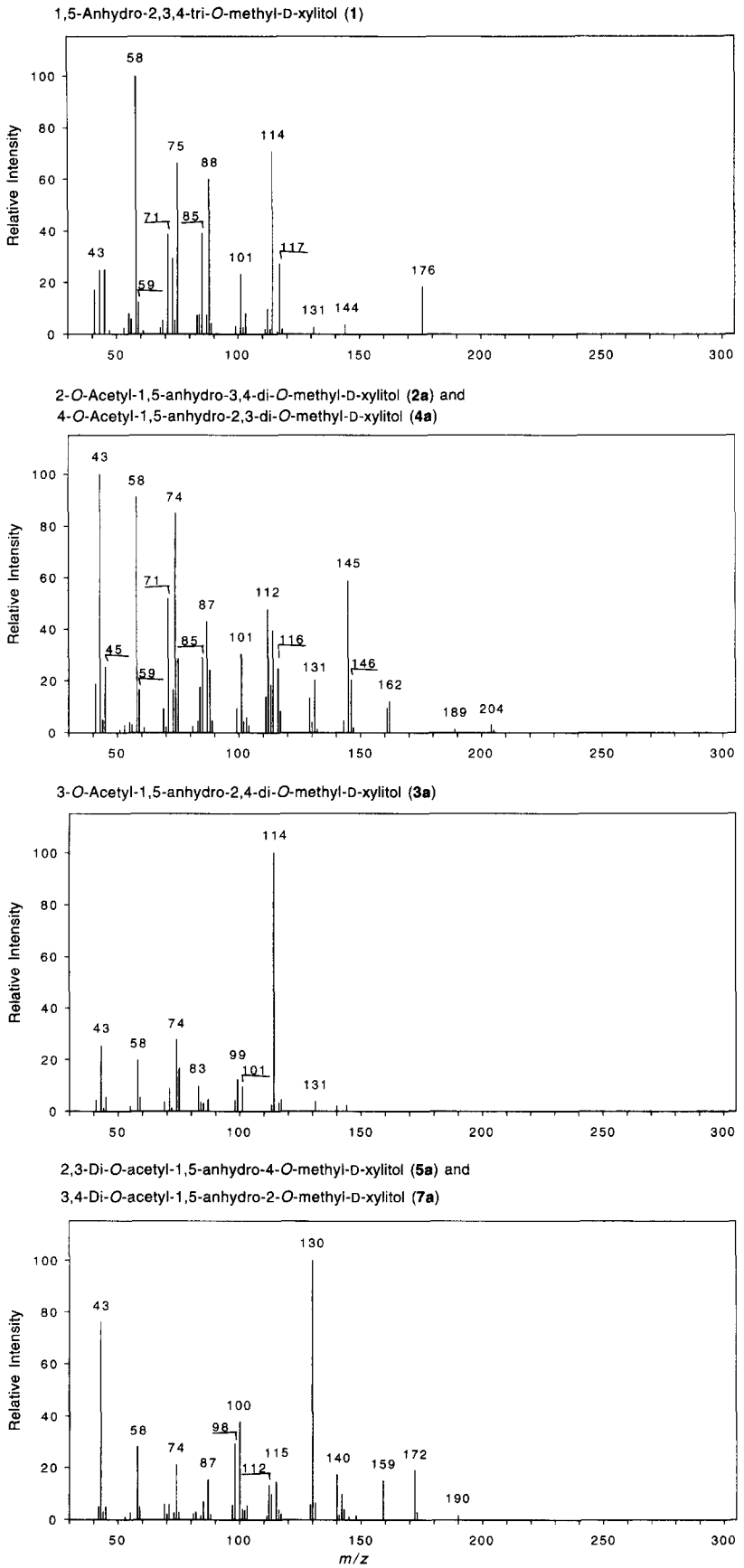


Fig. 1. Electron-ionization mass spectra of the methylated 1,5-anhydro-D-xylitol acetates (compounds **1** and **2a–8a**).

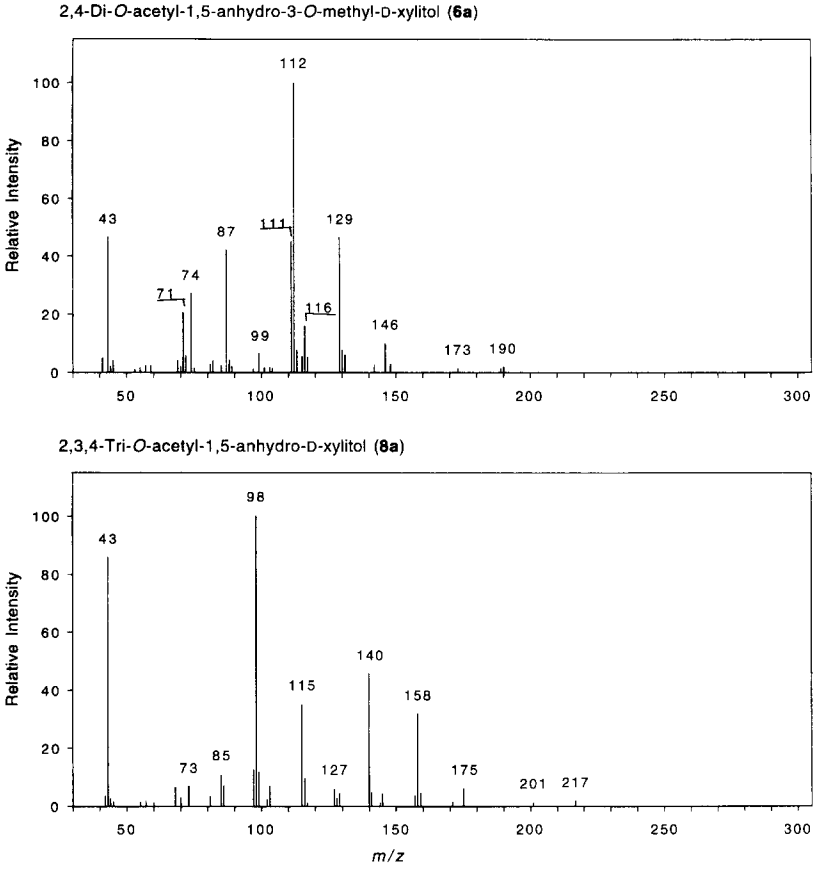


Fig. 1 (continued).

spectroscopy. A portion of each benzoate was then debenzoylated (NaOMe in MeOH), and the product was acetylated, affording the partially methylated 1,5-anhydro-D-xylitol acetate in chromatographically pure form.

^{1}H NMR spectra of partially methylated 1, 5-anhydro-D-xylitol benzoates (**2b**–**8b**).—Given in Table 2 are ^{1}H NMR spectral data for compounds **2b**–**8b**. The individual components of the mixture (see Table 2) were easily identified based upon a

Table 3
Linear temperature-programmed gas chromatography retention indices (LTPGLCRI) of compounds **1** and **2a**–**8a** [a]

Compound (position of acetyl)	Stationary phase		
	DB-5	DB-17	RT_x-200
1 (none)	1136.43 [b]	1312.32	1269.83
2a, 4a (2-, and 4-)	1318.76	1538.63	1597.93
3a (3-)	1346.35	1610.02	1679.09
5a, 7a (2,3-, and 3,4-)	1443.72	1721.24	1836.89
6a (2,4-)	1479.89	1735.05	1888.81
8a (2,3,4-)	1557.60	1843.92	2043.86

[a] Indices were determined using a mixture of all compounds co-injected with the homologous series of *n*-alkanes from $C_{11}H_{24}$ to $C_{26}H_{54}$. Values were calculated from the equation $LTPGLCRI_{(x)} = 100n + [100 \cdot \Delta n \cdot (t_{R(x)} - t_{R(n)})/(t_{R(n+\Delta n)} - t_{R(n)})]$ where $LTPGLCRI_{(x)}$ is the linear temperature-programmed gas–liquid chromatography retention index of the compound of interest (x), n is the carbon number of the *n*-alkane standard eluting just before the compound of interest (x), Δn is the difference in carbon number between the *n*-alkane standard eluting just before and just after the compound of interest (x), $t_{R(x)}$ is the absolute retention time of the compound of interest (x), and $t_{R(n)}$ and $t_{R(n+\Delta n)}$ are the absolute retention times of the *n*-alkanes eluting just before and just after the compound of interest (x). The temperature program for all columns was 80–250 °C at 2 °C/min with no initial hold time.

[b] Values are listed according to increasing retention index on the DB-5 column.

straightforward analysis of the chemical shifts and coupling constants of the ring hydrogen resonances. All resonances displayed the multiplicities and coupling constants expected for a tetrahydropyran derivative of the D-*xylo* configuration in the $^4C_1$ conformation and, in addition, the positions of substitution of benzoyl groups were readily discerned based upon the large downfield shift of the respective ring hydrogen resonances.

Since the parent compound, 1,5-anhydro-D-xylitol, is a meso compound, the 2-*O*-benzoyl **2b** and 4-*O*-benzoyl **4b** derivatives are enantiomeric, as are the 2,3-di-*O*-benzoyl **5b** and 3,4-di-*O*-benzoyl **7b** derivatives. Hence, these pairs of enantiomers are not distinguishable by ^{1}H NMR spectroscopy or GLC. Furthermore, the 3-*O*-benzoyl **3b** and 2,4-di-*O*-benzoyl **6b** derivatives are also meso compounds, so each contains three pairs of enantiotopic hydrogens, i.e., H-1e and H-5e, H-1a and H-5a, and H-2 and H-4. Each pair of enantiotopic hydrogens exhibited single resonances whose integrated areas corresponded to two protons.

*Mass spectra of the methylated 1,5-anhydro-*D*-xylitol acetates* (**1**,**2a–8a**).—Compounds **1** and **2a–8a** were analyzed by chemical-ionization (CI) mass spectrometry with ammonia as the reagent gas and by EI mass spectrometry. The CI (NH_3) mass spectra of all compounds displayed the expected $(M + H)^+$ and $(M + NH_4)^+$ ions, which, because of their unique molecular weights, readily identifies them as anhydropentitol derivatives. The EI mass spectra of the compounds are shown in Fig. 1. Although fragmentation pathways for 1,5-anhydropentitol derivatives have not been established, it is clear from inspection of these mass spectra that they are diagnostically different.

*GLC retention indices of methylated 1,5-anhydro-*D*-xylitol acetates* (**1**,**2a–8a**).—Given in Table 3 are the linear temperature-programmed gas–liquid chromatography retention indices [8] (LTPGLCRI) values for compounds **1** and **2a–8a** determined on three different capillary columns [4], one (DB-5) a relatively nonpolar stationary phase (5% phenyl–95% methyl polysiloxane), one (DB-17) a more polar stationary phase (50% phenyl–50% methyl polysiloxane), and one (RT_x-200) a relatively polar stationary phase (50% trifluoropropyl–50% methyl polysiloxane). Analyses were performed in triplicate on each column using a mixture of all six compounds and a mixture of *n*-alkanes from $C_{11}H_{24}$ to $C_{26}H_{54}$ as retention index standards. All standard deviations were less than 0.1.

3. Discussion

This is another in a series of papers describing the synthesis and spectral characterization of authentic standards for the reductive-cleavage method. The goal of these studies is to provide such data for standards representing all possible combinations of position(s) of linkage and ring form for the most frequently encountered sugars. Described herein is the synthesis of standards for D-xylopyranosyl residues, which are commonly encountered in the glycoproteins of plants [9,10], animals [11,12], and microorganisms [13,14], in saponins [15], and in plant polysaccharides [16,17].

In order to prepare such standards, a simple, rapid method for their synthesis was needed. We have previously shown that these requirements are easily met by a strategy [4] involving partial methylation of the parent anhydroalditol followed by benzoylation or, alternatively, by a strategy [18] involving partial benzoylation followed by methylation. In the present case, the former strategy was successful and all of the possible positional isomers of methylated and benzoylated 1,5-anhydro-D-xylitol were obtained. However, owing to the symmetry of the parent anhydroalditol, two pairs of products, i.e., the 2-benzoate **2b** and 4-benzoate **4b** and the 2,3-dibenzoate **5b** and the 3,4-dibenzoate **7b** are enantiomers and are thus not distinguishable by spectroscopic means. Therefore, using these standards it is not possible to distinguish between 2-linked and 4-linked D-xylopyranosyl residues or 2,3-linked or 3,4-linked D-xylopyranosyl residues. Should such residues be encountered, however, a distinction between the two possibilities could be made by conducting reductive cleavage in the presence of a deuterated reducing agent [19], isolating the product as its benzoate by HPLC, and characterizing the latter by ^{1}H NMR spectroscopy. Alternatively, 2-linked and 4-linked or 2,3-linked and 3,4-linked D-xylopyranosyl residues could be distinguished by standard methylation analysis by employing sodium borodeuteride to reduce the partially methylated aldoses [20].

For the benefit of those who use the reductive-cleavage method, the GLC retention indices of all standards were determined on three columns with differing stationary phases. As the data base of reductive-cleavage standards has grown, it has become apparent that the probability is great of two or more compounds having very similar retention data on one and even two different stationary phases. As described by Elvebak [21], combining the accuracy and precision of retention indices [22] with the superior

differentiation power of a three-stationary-phase approach [23] ensures that retention data will be reliable and unambiguous.

4. Experimental

General.—Reagents, solvents and starting materials were prepared as previously described [4]. Alkane standards were obtained from Aldrich Chemical Company. A stock solution of the homologous series of alkanes from $C_{11}H_{24}$ to $C_{26}H_{54}$ was prepared by combining 20–30 mg of each alkane and diluting to 10 mL with hexane.

Instrumentation.—HPLC was performed using a Beckman model 338 System Gold chromatograph. Reversed-phase chromatography was performed on a 5-μm particle-size Rainin Dynamax Microsorb semipreparative C_{18} reverse phase column (1.0 × 25 cm) equipped with a guard column (1.0 × 5 cm) having the same packing. The system was fitted with a 2.0-μm stainless steel in-line filter frit installed between the solvent mixing chamber and the injector and a 0.50-μm stainless steel filter frit installed between the injector and the guard column. The column was monitored with a UV detector set at 254 nm.

Analytical GLC was performed on a Hewlett–Packard 5890 gas–liquid chromatograph equipped with two split/splitless injection ports, two flame ionization detectors, and a Perkin–Elmer Nelson 1020X Dual Channel Personal Integrator. The columns used were a J&W Scientific DB-5 fused silica capillary column (0.25 mm × 30 m, 0.25-μm film thickness, 5% phenyl–95% methyl polysiloxane stationary phase), a J&W DB-17 fused silica capillary column (0.25 mm × 30 m, 0.25-μm film thickness, 50% phenyl–50% methyl polysiloxane stationary phase), and a Restek RT_x-200 fused silica capillary column (0.25 mm × 30 m, 0.25-μm film thickness, 50% trifluoropropyl–50% methyl polysiloxane stationary phase). Each column was fitted with a J&W deactivated fused silica capillary guard column (0.25 mm × 1 m) via a press-tight connector (either J&W or Restek). Chromatography on the DB-5 and RT_x-200 columns was performed simultaneously by fitting these columns and a guard column into a two-way (Y) press-tight capillary column splitter (Restek); the guard column was installed in the injection port. The injector and detector temperatures were set at 250 °C and 275 °C, respectively. Helium was used as the carrier gas at measured linear velocities (methane injection, oven temperature 80 °C) of 26.1, 28.4 and 27.8 cm/s, respectively, for the DB-5, DB-17 and RT_x-200 columns. The temperature program for all columns, which was optimized according to the guidelines set by Krupcik et al. [24], was 80–250 °C at 2 °C/min with no initial hold time.

GLC–MS analyses were performed using a Finnegan MAT 95 high-resolution double-focusing, reverse-geometry mass spectrometer equipped with a Hewlett–Packard 5890A Series II gas chromatograph and a DEC model 2100 workstation. Chemical-ionization mass spectra were acquired with NH_3 as the reagent gas at a source temperature of 180 °C, and NH_3 was introduced at a pressure of 4×10^{-4} Torr as indicated on the source ionization gauge. For CI spectra, the instrument was scanned from *m/z* 60–650 at 1 s/decade. Electron-ionization mass spectra were obtained at an ionization energy of 70 eV and at a source temperature of 200 °C. For EI spectra, the instrument was scanned from *m/z* 20–650 at 1 s/decade. The accelerating voltage was 5 kV. Both CI and EI spectra were acquired at a resolution of 1000 (10% valley definition).

^{1}H NMR spectra were recorded on a Varian VXR-500S NMR spectrometer in $CDCl_3$ as the solvent and were referenced to internal tetramethylsilane.

*Partially methylated 1,5-anhydro-*D*-xylitol benzoates* (**2b** – **8b**).—1,5-Anhydro-D-xylitol (60 mg), prepared by the method of Ness et al. [25], was dissolved in 3 mL of dry Me_2SO in a flame-dried 10-mL conical flask. Two 1-mL aliquots of this solution were removed and added separately to flame-dried 10-mL conical flasks. To each reaction was added 0.75, 1.5, and 2.5 equiv, respectively, of lithium methylsulfinylmethanide. The reaction mixtures were then subjected to methylation and benzoylation as previously described [4].

Separation of the above mixture of benzoates **2b**–**8b** was accomplished by reversed-phase HPLC (Table 1) using a semipreparative C_{18} column. Aliquots (20 μL) of the mixture were applied to the C_{18} column, which was equilibrated in 50:50 MeCN–H_2O at 3.0 mL/min. After injection, the column was eluted for 10 min, then programmed with a linear gradient to 95:5 MeCN–H_2O over 20 min. The individual components from eight or more applications were collected and combined and, after removal of solvent by evaporation under vacuum, were dissolved in $CDCl_3$ and identified by ^{1}H NMR spectroscopy.

*Methylated 1,5-anhydro-*D*-xylitol acetates* (**1**,**2a**–**8a**).—Approximately one-third to one-half of each

pure benzoate, obtained as described above, was debenzoylated and acetylated as previously described [4] to afford the partially methylated 1,5-anhydro-D-xylitol acetate standards in pure form. The pure standards were then chromatographed individually on the three aforementioned GLC columns under the conditions already described, except that the temperature of the columns was programmed from 80–250 °C at 6 °C/min. In this way, the relative orders of elution of the standards on each column were determined. In order to expedite acquisition of their mass spectra, further studies used mixtures of the standards prepared by acetylation of portions of the partial methylation reactions that were saved. The latter mixtures were also found to contain the tri-*O*-methyl derivative **1**, whose position of elution was verified by chromatography of an independently synthesized sample.

*Determination of LTPGLCRI values of methylated 1,5-anhydro-*D*-xylitol acetates* (**1**,**2a**–**8a**).—In order to ensure that the mixture of standards contained only the title compounds, aliquots of the individual pure standards were combined such that the integral of the area (flame ionization detection) of each component was at least 5% of the area of the most abundant component. An aliquot of the stock solution of *n*-alkanes from $C_{11}H_{24}$ to $C_{26}H_{54}$ was diluted 20-fold with hexane, then amounts of the alkane standard solution and the methylated anhydroalditol acetate standard solution were chosen for injection such that their area responses were comparable. Typically, a 1.0-μL Hamilton syringe was loaded sequentially with 0.05 μL $CHCl_3$, 0.05 μmL air, 0.1 μL alkane standard solution, 0.05 μL air, 0.5 μL methylated anhydroalditol acetate standard solution, and 0.1 μL air, then injected. The manner of loading the syringe was that recommended by the manufacturers of the GLC columns. Immediately after injection, the temperature program for the column was begun. LTPGLCRI values were determined in triplicate on each of the columns using the equation given in Table 3.

Acknowledgements

The authors thank Dr. Edmund Larka and Sean Murray for performing GLC–MS analyses. This investigation was supported by Grant GM34710, awarded by the Department of Health and Human Services.

References

[1] D. Rolf and G.R. Gray, *J. Am. Chem. Soc.*, 104 (1982) 3539–3541.
[2] G.R. Gray, *Methods Enzymol.*, 138 (1987) 26–38.
[3] G.R. Gray, in R. Chandrasekaran (Ed.), *Frontiers in Carbohydrate Research*, Vol. 2, Elsevier, New York, 1992, pp 154–167.
[4] L.E. Elvebak II, T. Schmitt, and G.R. Gray, *Carbohydr. Res.*, 246 (1993) 1–11.
[5] I. Ciucanu and F. Kerek, *Carbohydr. Res.*, 131 (1984) 209–217.
[6] S. Hakomori, *J. Biochem (Tokyo)*, 55 (1964) 205–208.
[7] C. Horvath and H.-J. Lin, *J. Chromatogr.*, 126 (1976) 401–420.
[8] H. van den Dool and P.D. Kratz, *J. Chromatogr.*, 11 (1963) 463–471.
[9] N. Bando, H. Tsuji, R. Yamanishi, and N. Nio, *Biosci., Biotechnol., Biochem.*, 60 (1996) 347–348.
[10] K. Hino, S. Yamamoto, O. Sano, Y. Taniguchi, K. Kohno, M. Usui, S. Fukuda, H. Hanzawa, H. Yaruyama, and M. Kurimoto, *J. Biochem. (Tokyo)*, 117 (1995) 289–295.
[11] J.A. van Kuik, H. van Halbeek, J.P. Kamerling, and J.F.G. Vliegenthart, *J. Biol. Chem.*, 260 (1985) 13984–13988.
[12] J.A. van Kuik, R.P. Sijbesma, J.P. Kamerling, J.F.G. Vliegenthart, and E.J. Wood, *Eur. J. Biochem.*, 160 (1986) 621–625.
[13] N. Kolarova, M. Gresik, and I. Smondrkova, *Chem. Pap.*, 49 (1995) 215–219.
[14] S. Merello, M. Xavier, P. Tosta, and J. Armando, *J. Biol. Chem.*, 269 (1994) 20294–20298.
[15] Y. Shao, B.N. Zhou, K. Ma, W. Kan, and M. Hou, *Chin. Chem. Lett.*, 5 (1994) 839–842.
[16] N.J. Stacey, K. Roberts, N.C. Carpita, B. Wells, and M.C. McCann, *Plant J.*, 8 (1995) 891–906.
[17] W.S. York, A.G. Darvill, M. McNeil, T.T. Stevenson, and P. Albersheim, *Methods Enzymol.*, 118 (1984) 3–41.
[18] N. Wang and G. R. Gray, *Carbohydr. Res.*, 274 (1995) 45–58.
[19] D. Rolf, J. A. Bennek, and G. R. Gray, *J. Carbohydr. Chem.*, 2 (1983) 373–383.
[20] H. Björndal, C. G. Hellerqvist, B. Lindberg, and S. Svensson, *Angew. Chem. Int. Ed. Engl.*, 9 (1970) 610–619.
[21] L.E. Elvebak II, Ph.D. Thesis, University of Minnesota (1994) 157–170.
[22] M.V. Budagehyi, E.R. Lombosi, T.S. Lombosi, S.Y. Mészáá, S. Nyiredy, G. Tarján, I. Timár, and J.M. Takács, *J. Chromatogr.*, 271 (1983) 213–307.
[23] G. Guiochon and C.L. Guillemin, *Quantitative Gas Chromatography*, Elsevier, New York, 1988, 484 pp.
[24] J. Krupcik, P. Cellar, D. Robpka, J. Garaj, and G. Giouchon, *J. Chromatogr.*, 351 (1986) 11–121.
[25] R.K. Ness, H.G. Fletcher, and C.S. Hudson. *J. Am. Chem. Soc.*, 72 (1950) 4547–4549.