

Carbohydrate Research 303 (1997) 293–302

CARBOHYDRATE RESEARCH

# *manno-* and *altro-*Sucrose, and some amino-analogues <sup>1</sup>

Frieder W. Lichtenthaler \*, Stefan Mondel

Institut für Organische Chemie, Technische Universität Darmstadt, Petersenstraße 22, D-64287 Darmstadt, Germany

Received 9 April 1997; accepted 25 May 1997

### Abstract

Preparatively useful procedures were developed for the conversion of sucrose into isomers with *manno*- and *altro*-configuration in the pyranoid moiety. The key compound was the 2-triflate-heptaacetate, generated from the readily accessible 3,4,6,1',3',4',6'-hepta-O-acetylsucrose by standard triflation.  $S_N$ 2-Displacement on the triflate by acetate ion ( $\rightarrow$  *manno*sucrose) or azide ion ( $\rightarrow$  *manno*-sucrosamine) proceeded in high yields, and on exposure to deacetylation conditions displacement was effected by the liberated 3-OH resulting in the *manno*-sucrose-2,3-epoxide; ring opening of the latter epoxide with water, ammonia, or azide proceeded in diaxial fashion to provide *altro*-sucrose, and its 3-amino and 3-azido derivatives, respectively. Sweetness evaluations proved *manno*-sucrose to be about 5 times less sweet than sucrose, whereas the *altro*-isomer was devoid of sweetness, correlating well with our refined AH-B-X structure-sweetness concept. © 1997 Elsevier Science Ltd.

Keywords: manno-Sucrose; altro-Sucrose; manno-Sucrose-2,3-epoxide; manno-Sucrosamine

## 1. Introduction

Sucrose (1), affectionately termed "the royal carbohydrate" [1], has for centuries been the world's most abundantly produced organic compound, and this in unparalleled purity. Its chemistry, although fairly well developed [2], has not been studied as extensively as that of its component sugars, D-glucose and D-fructose. The reasons for this lie in the chemical limitations imposed by the instability of the gly-

cosidic linkage under even slightly acidic conditions, which causes hydrolysis to occur either before or during the reaction, and its "over-functionalization" with hydroxyl groups of similar or identical reactivity meaning that regioselective derivatization is difficult to achieve. This is especially true for chemical modification at the secondary hydroxyl groups, as acylations [2–4] and alkylations [2,5–7] usually occur preferentially at the primary hydroxyl groups. Only upon careful mono-deprotonation of sucrose in aprotic solvents, e.g. NaH in DMF or pyridine, and trapping of the resulting sucrose 2-alkoxide by special heterocyclic acylation reagents [8] or by benzyl bromide [9], can reasonably high selectivities towards the 2-O-substituted derivatives be achieved. Of con-

<sup>&</sup>lt;sup>\*</sup> Corresponding author.

<sup>&</sup>lt;sup>1</sup> Presented in part at the XVIIIth International Carbohydrate Symposium, Milano, Italy, July 1996; Abstract BP 118.

siderable preparative utility proved to be the 2-Obenzyl-sucrose 2 thus obtained, as it can readily be converted, through acetylation and hydrogenolysis, into the sucrose heptaacetate 3 with the 2-OH group of the glucosyl moiety free, a key compound for the preparation of C-2-modified derivatives such as 2-oxo- and 2-deoxy-sucrose, and sucrosamine [9]. In this communication we wish to report the further exploitation of the sucrose heptaacetate 3 for the preparation of *manno*- and *altro*-sucrose, and the synthetically highly versatile *manno*-sucrose-2,3epoxide.

## 2. Results and discussion

Accessible from sucrose in 3 steps in a 42% overall yield [9], the hepta-O-acetyl-sucrose 3 with its free 2-OH group was considered a useful intermediate for effecting displacements at C-2 after the intro-

duction of suitable leaving groups. However, the respective 2-O-mesyl derivatives 4 and 5, readily prepared under standard conditions, proved to be unsuited for these purposes, as they are highly stable even towards forcing displacement conditions, for example caesium acetate in boiling toluene or sodium azide in refluxing DMF. In contrast, the corresponding sucrose 2-triflate 6, smoothly obtained (79%) by exposure of 3 to triflic anhydride in pyridine, was sufficiently reactive to enable displacement reactions. Thus, on refluxing in toluene with caesium acetate [10] it gave the octaacetate of manno-sucrose (7), which upon deacetylation afforded the unprotected disaccharide 8. Exposure of triflate 6 to sodium azide in dimethylsulfoxide for 2.5 h at 60 °C gave the 2-azido-2-deoxy-manno-sucrose heptaacetate 9, which was readily converted into the mannosucrosamine derivatives 10-12 by hydrogenation, acetylation, and de-O-acetylation (Scheme 1).



Scheme 1.

The exposure of triflate **6** to standard de-O-acetylation conditions (NaOMe/MeOH) proved to be preparatively particularly rewarding, as the glucose 3-OH, thereby liberated, effects an internal displacement of 2-triflate to form an oxirane ring, thus affording 2,3-anhydro-*manno*-sucrose **13**. For preparative purposes, **13** is advantageously prepared from the readily accessible sucrose heptaacetate **3** by combining the two steps — 2-O-triflation to **6** and ensuing NaOMe/MeOH treatment — to a one-pot operation; the overall yield of **13** then was a satisfactory 74%.

Oxirane ring opening in 13 with N-nucleophiles such as ammonia or azide proceeded smoothly and in the expected *trans*-diaxial fashion to provide the corresponding 3-amino-3-deoxy-altro-sucrose (14) or its 3-azido derivative 15, respectively. From 15, the 3-acetamido derivative 16 could be prepared by reduction with in situ N-acetylation. By contrast, epoxide opening with O-nucleophiles proved to be rather capricious, since standard or even mild alkaline conditions of various sorts gave complex product mixtures, probably arising from oxirane ring opening in the manno-2,3-epoxide 13 by methoxide, or by one of the hydroxyl groups of the fructose moiety, and/or by the 4-OH of 13 to give altro-3,4-epoxide and ensuing products. Applying conditions that were successful for the conversion of 2,3-anhydro- $\alpha$ cvclomannin into  $\alpha$ -cycloaltrin [11], i.e. heating in tri-distilled water (24 h at 75 °C), eventually gave the *altro*-sucrose 17, albeit in modest yield (20%); it could readily be characterized as such, e.g. by its 800-MHz spectrum (cf. Fig. 1) and as its octaacetate 18.

Configurational assignments.—Structural and configurational evidence for each of the new compounds described was secured by the <sup>1</sup>H and <sup>13</sup>C NMR spectra, which warrant little comment beyond the data given in the experimental section; e.g. mannosucrose (8) exhibited the expected small anomeric coupling ( $J_{1,2}$  1.8 Hz), whilst the 2,3-epoxide 13 showed the characteristics typical for 2,3-anhydro- $\alpha$ -D-mannopyranosides [12–16], i.e. a  $J_{2,3}$  of 3.8 Hz and zero values for  $J_{1,2}$  and  $J_{3,4}$ . Accordingly, the pyranoid ring in 13 adopts the <sup>0</sup> $H_5$  half-chair geometry.

The likely conformational preferences of the *altro*-sucroses **14–18** are less obvious as the  ${}^{4}C_{1}$  and  ${}^{1}C_{4}$  conformations of  $\alpha$ -altropyranoid chairs are very similar in stability [17], and could adopt either form, or, more likely, an equilibrium between the two. At 800 MHz (cf. Fig. 1), the  ${}^{1}$ H NMR spectrum of *altro*-sucrose **17** in D<sub>2</sub>O is of first-order and the readily acquirable coupling constants (see Table 1) — most notably a  $J_{1,2}$  of 4.2 and a  $J_{2,3}$  of 6.3 Hz — neither correspond to those expected for a  ${}^{4}C_{1}$  nor a  ${}^{1}C_{4}$  conformation, but lie in between, thus indicating



Fig. 1. <sup>1</sup>H NMR spectrum of *altro*-sucrose (17) at 800 MHz in D<sub>2</sub>O at 30 °C. Pyranoid ring couplings:  $J_{1,2}$  4.20,  $J_{2,3}$  6.30,  $J_{3,4}$  3.62, and  $J_{4,5}$  6.77 Hz.

the presence of a  ${}^{4}C_{1} \rightleftharpoons {}^{0}S_{2} \rightleftharpoons {}^{1}C_{4}$  conformational equilibrium whose position lies on the  ${}^{0}S_{2} \rightleftharpoons {}^{1}C_{4}$  side rather than the other (cf. Fig. 2). The same holds for the 3-amino-analogue **14** as it exhibits nearly identical couplings between the pyranoid hydrogens (cf. Table 1). However, in the case of 3-acetamido-*altro*-sucrose **16** ( $J_{1,2}$  3.6 Hz) and even more pronouncedly in the 3-azido derivative **15** ( $J_{1,2}$  2.5 Hz), the conformational equilibrium appears to be shifted towards the  ${}^{4}C_{1}$  side.

These rationalizations are corroborated by  ${}^{1}H^{-1}H$ couplings compiled in Table 1 for  $\alpha$ -D-altropyranose, its methyl glycoside, and various cyclo-oligosaccharides with  $\alpha$ -(1  $\rightarrow$  4)-linked altropyranose residues. They clearly give evidence that the position of the conformational  ${}^{4}C_{1} \rightleftharpoons {}^{1}C_{4}$  equilibrium in water can vary within the entire range of intermediate conformations, whereby, conceivably, the nature of the first water shell around the molecules is the determining factor. Methyl  $\alpha$ -D-altropyranoside, with a  $J_{1,2}$  of 2.3 Hz, is undoubtedly in the  ${}^{4}C_{1}$  conformation in aqueous solution, whilst in the case of  $\alpha$ -D-altropyranose  $(J_{1,2} 3.4 \text{ Hz})$  and, more pronouncedly, with the *al*tro-sucrose and  $\alpha$ - and  $\beta$ -cycloaltrins ( $J_{1,2}$  4.2, 4.5, and 4.7 Hz) the conformational equilibrium is increasingly shifted from the  ${}^{4}C_{1}$  geometry towards the skew  ${}^{0}S_{2}$  form as a pseudorotational intermediate. Most interesting in this context are the last four entries in Table 1, referring to  $\alpha$ - and  $\beta$ -cyclodextrin derivatives in which one  $\alpha$ -(1  $\rightarrow$  4)-linked glucose unit has been chemically converted into altrose, 3-amino-3-deoxy-altrose and 3-alkylthio-3-deoxy-altrose, respectively; they show unusually large values for  $J_{1,2}$  (6.6–6.9 Hz) and  $J_{2,3}$  (10.5 and 11.2 Hz for

Table 1 Pyranoid ring coupling constants in  $D_2O$  of  $\alpha$ -D-altropyranose and various of its derivatives [11,18–22]

	Conformation	α-D-Altropyranose				Coupling constants [Hz] <sup>a</sup>				Ref.
		X	R	R'		J <sub>1,2</sub>	J <sub>2,3</sub>	J <sub>3,4</sub>	$J_{4,5}$	_
${}^{4}C_{1}$	$RO \xrightarrow{HO}OH \\ H^3 \xrightarrow{H^2}H^1 \\ X \xrightarrow{H^2}OR'$	OH	Н	CH3		2.3				
		OH	Η	Н		3.4 <sup>b</sup>	5.5°			
		NHAc	Н	Fru <sup>d</sup>	(16)	3.6	5.9	4.2	4.2	
	1,	ОН	Н	Fru <sup>d,e</sup>	(17)	4.20	6.30	3.62	6.77	
<sup>0</sup> S <sub>2</sub>	$RO \rightarrow H^{3} \rightarrow O \rightarrow H^{1} \rightarrow O \rightarrow OH \rightarrow OH^{2} \rightarrow OH^$	$\mathrm{NH}_2$	Н	Fru <sup>d</sup>	(14)	4.3	6.5	4.0	6.8	
		ОН	$-(Altp)_6-$			4.5	7.8	3.7	5.8	[18]
		OH	$-(Altp)_5 - e^{e}$			4.73	8.19	3.71	5.32	[11]
		ОН	$-(\operatorname{Glc} p)_6 - {}^{\mathrm{f}}$			6.6				[19]
${}^{1}C_{4}$	RO X H2 H1 OR' OR' OH H1 OR' OH H3 O' OH H3 O'	NHAc	$-(\operatorname{Glc} p)_6 - {}^{\mathrm{f}}$			6.8				[20]
		$\mathrm{NH}_2$	$-(\operatorname{Glc} p)_5 - {}^{\mathrm{f}}$			6.9	10.5	3.7		[21]
		SR	- (G	$lcp)_6 - f$			11.2	3.4		[22]

<sup>a</sup> Blank spaces denote that J values at 300–500-MHz level could not reliably be inferred from complex multiplets. <sup>b</sup> In addition, a long-range coupling,  $J_{1,3}$  0.8 Hz, is observed, due to W arrangement of H-1 and H-3 in the  ${}^{4}C_{1}$  conformation.

<sup>c</sup> The assignment was verified by selective TOCSY, phase sensitive COSY, and ECOSY ( $\pm 0.3$  Hz).

<sup>d</sup> Fru =  $\beta$ -D-Fructofuranosyl.

<sup>e</sup> 800-MHz data.

<sup>f</sup> The abbreviations refer to  $\alpha$ - and  $\beta$ -cyclodextrin derivatives in which one  $\alpha$ -(1  $\rightarrow$  4)-linked glucose unit has been chemically converted into D-altrose, 3-amino-3-deoxy-D-altrose, and 3-alkylthio-3-deoxy-D-altrose, respectively.



Fig. 2. The chair/half-chair/skew (twist-boat) pseudorotational itinerary between D-altropyranoid rings in  ${}^{4}C_{1}$  and  ${}^{1}C_{4}$  conformation. Due to the comparatively large  $J_{1,2}$  and  $J_{2,3}$  values found for *altro*-sucrose **17** (4.2 and 6.3 Hz, respectively, in D<sub>2</sub>O at 30 °C), the conformational equilibrium in aqueous solution lies on the  ${}^{1}C_{4} \rightleftharpoons {}^{3}H_{2} \rightleftharpoons {}^{0}S_{2}$  side rather than on the other. The same holds for the 3-amino– and 3-acetamido-analogues **14** and **16**.

the two available cases), which unequivocally prove the equilibrium to lie nearly fully on the  ${}^{1}C_{4}$  side.

That the position of the conformationally equilibrium within the  ${}^{4}C_{1} \rightleftharpoons {}^{0}S_{2} \rightleftharpoons {}^{1}C_{4}$  pseudorotational itinerary (cf. Fig. 2) is strongly dependent on the hydrogen-bonding pattern of the sugar hydroxyls to the water molecules within the first hydration shell, is substantiated by distinctly different coupling constants in other solvents, or when the OH-groups are fully protected, e.g. by acetylation. Thus,  $\alpha$ -D-altropyranose in methanolic solution shows a  $J_{1,2}$  of 1.9 Hz (vs. 3.4 Hz in water), indicating the equilibrium to shift to the  ${}^{4}C_{1}$  geometry in less solvating solvents. The same is observed for its pentaacetate [23] and the *altro*-sucrose octaacetate (18), which exhibit in CDCl<sub>3</sub> nearly identical coupling patterns  $(J_{1,2} \ 1.3, \ J_{2,3} \ \text{and} \ J_{3,4} \approx 3.5, \ J_{4,5} \ 9.3 \ \text{and} \ 10.0 \ \text{Hz},$ respectively), evidence for the adoption of an essentially perfect  ${}^{4}C_{1}$  conformation. Accordingly, the 1,3-diaxial repulsion of O-1 and O-3 in  $\alpha$ -D-altropyranoid rings is, interestingly, larger between solvated free OH-groups in a water shell than between acetoxy groups in 1,3-diaxial disposition.

Sweetness evaluation.—As the relative sweetness of configurational isomers of sucrose are to have bearing on assessing structure-sweetness relationships, the manno- (8) and altro-sucrose (17) prepared

here, as well as the 2-deoxy-sucrose, which has recently become readily accessible [9], were evaluated for their intensity to elicit the sensation of sweetness. An ad hoc tasting panel was established, pre-trained with standards for several consecutive days, and then given 5% aqueous solutions of **8** and **17**, and 10% solution of 2-deoxy-sucrose to evaluate comparatively against 1% and 2% solutions of sucrose. There was fairly uniform agreement that 2-deoxy-sucrose is about 10 times less sweet than sucrose, its *manno*configurational isomer about half as sweet as the parent compound, whereas *altro*-sucrose, in the concentration tested, is devoid of sweetness.

It is of interest to assess these data in the context of the modified AH-B-X concept recently advanced [24,25], which emerged from extensive molecular modelings of sucrose, of various sucrose derivatives, and of non-carbohydrate sweeteners, most notably the generation of their molecular electrostatic potentials (MEPs) and their molecular lipophilicity patterns (MLPs). For sucrose, the AH-B-X sites docking at and interacting with a complementary tripartite binding site in the taste bud receptor, have been assigned to the glucosyl 2-OH (AH, hydrogen-bond donor) and 3-OH (B, H-bond acceptor) as depicted in Fig. 3, whereas the hydrophobic X-part is represented by the entire back side of the fructose portion. Another steric requirement for eliciting sweetness emerged to be the opposite side arrangement of hydrophobic and hydrophilic regions within a sweetener [25].

According to this concept, the glucosyl 2-OH, as the AH-part, is essential for engaging in hydrogen bonding to the receptor side, hence its configurational inversion ( $\rightarrow$  manno-sucrose) or its removal altogether ( $\rightarrow$  2-deoxy-sucrose) should result in substantial decrease of sweetness. Configurational changes at both, the AH- and B-parts of the glucophore, as achieved by inversion of the glucosyl 2- and 3-OH



Fig. 3. Location of the tripartite AH-B-X glucophore ("sweetness triangle") in sucrose [25,26].

groups ( $\rightarrow$  altro-sucrose) should interfere even more intensely with the sweet receptor interaction. That manno-sucrose is 5 times less, and altro-sucrose devoid of sweetness gives substantial credence to the relevance and predictive value of this concept.

## 3. Experimental

General methods.-Melting points were determined with a Bock hot-stage microscope and are not corrected. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. Mass spectra were recorded with a Varian 311 a spectrometer and NMR spectra with Bruker WM 300 and AC 300 spectrometers at 305 K unless otherwise stated, and chemical shifts are given in ppm using  $Me_4Si$  (in CDCl<sub>3</sub>) and sodium - 2, 2, 3, 3-tetradeutero - 3-trimethylsilvlpropionate (in  $D_2O$ ) as internal standards. All signals have been assigned using 2D-NMR techniques. Tlc on Silica Gel 60  $F_{254}$  plastic sheets (E. Merck, Darmstadt) was used to monitor the reactions and ascertain the purity of the products. Eluents employed: A = 2:1 EtOAc-toluene, B = 3:2toluene-EtOAc, C = 1:1 toluene-EtOAc, D = 6:1MeCN-water, E = 10:1 MeCN-water. The spots were visualized by UV light or by spraying with 50%  $H_2SO_4$  and charring at 120 °C for 5 min. Column chromatography was performed on Silica Gel 60 (Macherey & Nagel; 63–200 nm). Evaporations were conducted under diminished pressure at bath temperatures below 45 °C. The molecular sieves used were freshly desiccated, ion-exchange resins used were thoroughly pre-washed with dry MeOH.

1,3,4,6-Tetra-O-acetyl-B-D-fructofuranosyl 3,4,6-tri-O-acetyl-2-O-methanesulfonyl- $\alpha$ -D-glucopyranoside (4, 2-O-mesyl-sucrose heptaacetate).—To a cooled soln (0 °C) of 2-OH free sucrose heptaacetate 3 [9] (467 mg, 0.65 mmol) in  $CH_2Cl_2$  (5 mL) was added pyridine (0.15 mL, 1.86 mmol) followed by dropwise addition of methanesulfonyl chloride (0.3 mL, 3.79 mmol). After stirring for 2 days at 0 °C the reaction mixture was quenched by ice-water, and the organic phase was successively washed with 4 M  $H_2SO_4$ (10 mL), 2 M NaHCO<sub>3</sub> (10 mL), and water. Drying  $(MgSO_4)$  and concn under reduced pressure afforded a brown syrup which was purified by elution from a silica gel column  $(2 \times 20 \text{ cm})$  with 1:1 toluene-EtOAc. Removal of the solvent from the eluate gave 4 (320 mg, 69%) as a hygroscopic, colorless foam;  $R_{\rm f}$  0.46 in A;  $[\alpha]_{\rm D}^{20}$  +54.6° (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.04–2.18 (7 s, 3 H each, 7 Ac), 3.10 (s, 3 H, SO<sub>2</sub>Me), 4.13–4.39 (m, 8 H, H-5, 2 H-6, 2 H-1', H-5', 2 H-6'), 4.68 (dd, 1 H, H-2), 5.09 (dd, 1 H, H-4), 5.38–5.51 (m, 3 H, H-3, H-3', H-4'), 5.72 (d, 1 H, H-1);  $J_{1,2}$  3.7,  $J_{2,3}$  10.4,  $J_{3,4}$  9.8,  $J_{4,5}$  9.6 Hz. <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  19.5–20.4 (CO*Me*), 37.4 (SO<sub>2</sub>Me), 60.5 (C-6), 62.1 (C-6'), 62.5 (C-1'), 67.2 (C-4), 67.6 (C-5), 68.3 (C-3), 72.9 (C-2), 73.6 (C-4'), 74.5 (C-3'), 78.0 (C-5'), 89.3 (C-1), 102.8 (C-2'), 168.3–169.6 (COMe). MS (FD, 15 mA): m/z 714, [M]<sup>+</sup>, 367, [triacetyl – 2-mesyl-glucopyranosyl]<sup>+</sup>, 331, [tetraacetyl – fructofuranosyl]<sup>+</sup>. Anal. Calcd for  $C_{27}H_{38}O_{20}S$ : C, 45.38; H, 5.36. Found: C, 45.70; H, 5.02.

 $\beta$ -D-Fructofuranosyl 2-O-methanesulfonyl- $\alpha$ -Dglucopyranoside (5, 2-O-mesyl-sucrose).—De-Oacetylation of 4 (236 mg, 0.33 mmol) was effected by exposure to NaOMe (178 mg, 3.3 mmol) in MeOH (15 mL) in the presence of molecular sieves (3 Å) for 15 min at ambient temperature. The reaction mixture was neutralized by addition of acidic ion-exchange resin (E. Merck I). Filtration and concn of the filtrate gave 130 mg (94%) of 5 as a colorless syrup;  $R_f$  0.44 in B;  $[\alpha]_{D}^{20}$  + 59.6° (c 1.0, MeOH); <sup>1</sup>H NMR (300 MHz,  $D_2O$ ):  $\delta$  3.30 (s, 3 H, SO<sub>2</sub>Me), 3.58 (dd, 1 H, H-4), 3.66 (s, 2 H, 2 H-1'), 3.76–3.93 (m, 6 H, H-5, 2 H-6, H-5', 2 H-6'), 3.98 (dd, 1 H, H-3), 4.03 (dd, 1 H, H-4'), 4.26 (d, 1 H, H-3'), 4.50 (dd, 1 H, H-2), 5.61 (d, 1 H, H-1);  $J_{1,2}$  3.7,  $J_{2,3}$  9.9,  $J_{3,4}$  9.5,  $J_{4,5}$  9.6,  $J_{3',4'}$  8.8,  $J_{4',5'}$  8.3 Hz. <sup>13</sup>C NMR (75.5 MHz, D<sub>2</sub>O): δ 38.2 (SO<sub>2</sub>Me), 60.5 (C-6), 61.5 (C-1'), 62.9 (C-6'), 69.7 (C-4), 70.7 (C-3), 72.8 (C-5), 74.4 (C-4'), 75.9 (C-3'), 79.6 (C-2), 82.1 (C-5'), 90.7 (C-1), 104.6 (C-2'). MS (FD, 20 mA): m/z 443, [MNa]<sup>+</sup>.

1,3,4,6-Tetra-O-acetyl-β-D-fructofuranosyl 3,4,6-tri-O -  $acetyl - 2 - O - trifluoromethanesulfonyl - \alpha - D$ glucopyranoside (6).—To a cooled soln (-25 °C) of  $3 (1.69 \text{ g}, 2.65 \text{ mmol}) \text{ in CH}_2 \text{Cl}_2 (120 \text{ mL}) \text{ under Ar}$ and containing molecular sieves (4 Å) was added pyridine (0.43 mL, 5.3 mmol) followed by the dropwise addition of trifluoromethanesulfonic anhydride (0.66 mL, 4 mmol). After stirring for 1.5 h the reaction mixture was filtered, washed with 2 M NaHCO<sub>3</sub> (50 mL) and dried (MgSO<sub>4</sub>). Concentration afforded a syrup which was purified by elution from a silica gel column ( $4 \times 25$  cm) with 1:1 toluene-EtOAc. Removal of the solvent from the eluate under reduced pressure gave 1.6 g (79%) of 6 as a syrup, unstable at ambient temperature, but stable at -20°C for several weeks without decomposition;  $R_f$  0.40 in C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 2.05-2.15 (7 s, 3 H each, 7 Ac), 4.14–4.42 (m, 8 H, H-5, 2 H-6,

2 H-1', H-5', 2 H-6'), 4.77 (dd, 1 H, H-2), 5.12 (dd, 1 H, H-4), 5.41 (dd, 1 H, H-4'), 5.50 (d, 1 H, H-3'), 5.56 (dd, 1 H, H-3), 5.89 (d, 1 H, H-1);  $J_{1,2}$  3.8,  $J_{2,3}$ 10.1,  $J_{3,4} = J_{4.5}$  9.8,  $J_{3',4'}$  6.4,  $J_{4',5'}$  6.6 Hz. <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  20.4–21.5 (CO*Me*), 61.1 (C-6), 62.7 (C-6'), 63.2 (C-1'), 68.0 (C-4), 68.2 (C-5), 68.9 (C-3), 73.9 (C-4'), 75.4 (C-3'), 78.7 (C-5'), 80.6 (C-2), 89.7 (C-1), 104.0 (C-2'), 118.4 (q, CF<sub>3</sub>,  $J_{C,F}$ 302 Hz), 169.7–170.6 (COMe).

1,3,4,6-Tetra-O-acetyl-B-D-fructofuranosyl 2,3,4,6tetra - O - acetyl -  $\alpha$  - D - mannopyranoside (7, manno sucrose-octaacetate).—To a stirred soln of triflate 6 (396 mg, 0.52 mmol) in dry toluene (25 mL) was added molecular sieves (4 Å), cesium acetate, and tetrabutylammonium acetate (1 g each). The mixture was refluxed for 2 h. Filtration, washing with water (5 mL), drying (MgSO<sub>4</sub>), concn under reduced pressure, and elution of the residual syrup from a silica gel column ( $4 \times 25$  cm) with 1:1 toluene-EtOAc afforded 270 mg (77%) of 7 as a syrup;  $R_f$  0.33 in C;  $[\alpha]_{D}^{20} + 8.8^{\circ}$  (c 0.7, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.99–2.17 (8 s, 3 H each, 8 Ac), 4.17–4.38 (m, 8 H. H-5, 2 H-6, 2 H-1', H-5', 2 H-6'), 5.13 (dd, 1 H, H-2), 5.27-5.37 (m, 2 H, H-3, H-4), 5.39-5.47 (m, 3 H, H-1, H-3', H-4');  $J_{1,2} = J_{2,3}$  2.4 Hz. <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 19.5–19.8 (COMe), 61.4 (C-6), 62.6 (C-6'), 62.7 (C-1'), 64.6 (C-3), 67.7 (C-4), 68.9 (C-5), 69.1 (C-2), 73.8, 75.1 (C-3', C-4'), 77.7 (C-5'), 90.3 (C-1), 102.5 (C-2'), 168.6-169.6 (COMe). MS (FD, 15 mA): m/z 678, [M]<sup>+</sup>, 619, [MH - MeCOOH]<sup>+</sup>, 347, [tetraacetyl - mannopyranosyl]<sup>+</sup>, 331, [tetraacetyl - fructofuranosyl]<sup>+</sup>. Anal. Calcd for C<sub>28</sub>H<sub>38</sub>O<sub>19</sub>: C, 49.54; H, 5.65. Found: C, 47.91; H, 5.35.

 $\beta$ -D-Fructofuranosyl  $\alpha$ -D-mannopyranoside (8, manno-sucrose).—De-O-acetylation of 7 (270 mg, 0.4 mmol) was effected by exposure to NaOMe (216 mg, 4 mmol) in MeOH (15 mL) under  $N_2$  in the presence of molecular sieves (3 Å). After 5 min stirring at ambient temperature, the reaction mixture was neutralized by addition of ion-exchange resin (amberlite IR-120, H<sup>+</sup>-form). Filtration and concn of the filtrate under reduced pressure gave 131 mg (quant.) of **8** as a colorless syrup;  $R_f = 0.29$  in D;  $[\alpha]_D^{20}$  $+19.1^{\circ}$  (c 1.2, H<sub>2</sub>O); <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O):  $\delta$ 3.66 (s, 2 H, 2 H-1'), 3.73-3.92 (m, 9 H, H-2, H-3, H-4, H-5, 2 H-6, H-5', 2 H-6'), 4.05 (dd, 1 H, H-4'), 4.16 (d, 1 H, H-3'), 5.35 (d, 1 H, H-1);  $J_{1,2}$  1.8,  $J_{3',4'}$ 8.7,  $J_{4',5'}$  8.0 Hz. <sup>13</sup>C NMR (75.5 MHz, D<sub>2</sub>O):  $\delta$ 63.5 (C-6), 63.8 (C-1'), 65.3 (C-6'), 69.3 (C-4), 73.0, 74.0, 76.1 (C-2, C-3, C-5), 76.8 (C-4'), 79.0 (C-3'), 84.4 (C-5'), 96.4 (C-1), 106.8 (C-2'). MS (FD, 20 mA): m/z 365, [MNa]<sup>+</sup>, 163, [mannopyranosyl]<sup>+</sup>, [fructofuranosyl]<sup>+</sup>. Anal. Calcd for C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>: C, 42.11; H, 6.48. Found: C, 40.06; H, 6.41.

1,3,4,6-Tetra-O-acetyl-β-D-fructofuranosyl 3,4,6-tri-O -  $acetyl - 2 - azido - 2 - deoxy - \alpha - D - mannopyranoside$ (9).—Triflate 6, prepared in situ from 189 mg (0.3)mmol) of sucrose heptaacetate 3, according to the procedure described above but without chromatographic purification, was dissolved in Me<sub>2</sub>SO (40) mL) followed by addition of molecular sieves (4 Å).  $NaN_{2}$  (0.6 g, 9 mmol) and tetrabutylammonium chloride (0.5 g) were added and the soln was heated at 60 °C for 2.5 h, followed by dilution with 100 mL of EtOAc and filtration. The mixture was washed with water  $(3 \times 30 \text{ mL})$ , dried (MgSO<sub>4</sub>), evaporated to dryness, and the residue was applied to a silica gel column ( $2 \times 20$  cm). Elution with 1:1 toluene–EtOAc and freeze drying of the eluate afforded 97 mg (50%) of **9** as a foam;  $R_f 0.29$  in C;  $[\alpha]_D^{20} + 12.9^{\circ}(c \ 0.8,$ CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.99–2.09 (7 s, 3 H each, 7 Ac), 3.89 (dd, 1 H, H-2), 4.08-4.26 (m, 8 H, H-5, 2 H-6, 2 H-1', H-5', 2 H-6'), 5.25–5.39 (m, 4 H, H-3, H-4, H-3', H-4'), 5.43 (d, 1 H, H-1);  $J_{1,2}$  2.1,  $J_{2,3}$  2.3 Hz. <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 20.5-21.5 (COMe), 61.9 (C-6), 62.2 (C-2), 62.7 (C-6'), 63.9 (C-1'), 65.4 (C-5), 69.9 (C-4), 70.8 (C-3), 74.1 (C-4'), 76.0 (C-3'), 78.4 (C-5'), 92.0 (C-1), 103.6 (C-2'), 169.5–170.7 (COMe). MS (FD): m/z662, [M]<sup>+</sup>, 602, [M – MeCOOH]<sup>+</sup>, 331, [tetraacetyl - fructofuranosyl]<sup>+</sup>, 314, [triacetyl - 2-azidomannopyranosyl]<sup>+</sup>. Anal. Calcd for  $C_{26}H_{35}O_{17}N_3$ : C, 47.20; H, 5.33; N, 6.35. Found: C, 45.94; H, 5.18; N, 5.82.

1,3,4,6-Tetra-O-acetyl-B-D-fructofuranosyl 3,4,6-tri-O-acetyl-2-amino-2-deoxy- $\alpha$ -D-mannopyranoside (10). -A soln of 9 (240 mg, 0.36 mmol) in EtOAc (15 mL) was hydrogenated over 10% Pd/C at ambient temperature for 4 days. Filtration and removal of the solvent left a syrup, which was purified by elution from a silica gel column with a gradient from EtOAc to 20:1 EtOAc-MeOH yielding 78 mg (33%) of 10 as a colorless syrup;  $R_{\rm f}$  0.21 in EtOAc;  $[\alpha]_{\rm D}^{20} - 5.4^{\circ}$  $(c 2.4, CHCl_3)$ ; <sup>1</sup>H NMR (300 MHz, CDCl\_3):  $\delta$ 1.97-2.08 (7 s, 3 H each, 7 Ac), 4.01-4.27 (m, 10 H, H-2, H-3, H-5, 2 H-6, 2 H-1', H-5', 2 H-6'), 4.88 (dd, 1 H, H-4), 5.31 (m, 2 H, H-1, H-4'), 5.39 (d, 1 H, H-3'), 6.35 (d, 2 H,  $NH_{2}$ );  $J_{3,4} = J_{4,5}$  6.6,  $J_{2,NH}$  7.6,  $J_{3',4'}$  6.9,  $J_{4',5'}$  6.8 Hz. <sup>13</sup>Č NMR (75.5 MHz, CDCl<sub>3</sub>): δ 19.2-21.1 (COMe), 54.1 (C-2), 63.0 (C-6), 63.6 (C-6'), 64.3 (C-1'), 68.0, 69.3 (C-3, C-4, C-5), 75.2 (C-4'), 75.8 (C-3'), 78.6 (C-5'), 92.6 (C-1), 103.5 (C-2'), 169.8–171.4 (COMe). MS (FD, 20 mA): m/z 636, [M]<sup>+</sup>, 331, [tetraacetyl – fructofuranosyl]<sup>+</sup>, 289, [triacetyl – 2-amino-glucopyranosyl]<sup>+</sup>.

1, 3, 4, 6 - Tetra - O - acetyl -  $\beta$  - D - fructofuranosyl 2 acetamido - 3, 4, 6 - tri - O - acetyl - 2 - deoxy - α - D mannopyranoside (11).—To a soln of 10 (70 mg, 0.11 mmol) in EtOAc (5 mL) stirred in an ice-bath was added Ac<sub>2</sub>O (0.6 mL) and a catalytic amount of DMAP. After 30 min, the reaction mixture was dild with additional 50 mL EtOAc and washed successively with 4 M  $H_2SO_4$  (10 mL), 2 M NaHCO<sub>3</sub> (10 mL), and water to a neutral reaction. The product was dried  $(MgSO_4)$  and removal of the solvent gave 52 mg (69%) of 11;  $R_f$  0.31 in EtOAc; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.99–2.19 (8 s, 3 H each, 8 Ac), 4.13-4.35 (m, 8 H, H-5, 2 H-6, 2 H-1', H-5', 2 H-6'), 4.50 (m, 1 H, H-2), 5.14 (dd, 1 H, H-4), 5.31–5.39 (m, 3 H, H-1, H-3, H-4'), 5.46 (d, 1 H, H-3'), 5.85 (d, 1 H, NHAc);  $J_{3,4} = J_{4,5}$  10.1,  $J_{2,NHAc}$ 8.8,  $J_{3'4'}$  6.5 Hz. <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$ 19.5-19.7 (7 COMe), 22.3 (NHCOMe), 50.1 (C-2), 61.4 (C-1'), 62.3 (C-6), 63.1 (C-6'), 64.6 (C-4), 67.7 (C-5), 68.4 (C-3), 74.1 (C-4'), 75.1 (C-3'), 77.8 (C-5'), 91.7 (C-1), 102.6 (C-2'), 168.7–169.6 (COMe).

β-D-Fructofuranosyl 2-acetamido-2-deoxy-α-Dmannopyranoside (12, N-acetyl-manno-sucrosamine). —To a soln of 51 mg (75 (mol) of 11 in MeOH (2 mL) molecular sieves (3 Å) and NaOMe (40.5 mg, 0.75 mmol) was added. After stirring for 5 min at room temperature the reaction mixture was neutralized by Amberlite IR-120 (H<sup>+</sup>-form). Filtration and removal of the solvent under reduced pressure gave 30 mg (quant.) of 12 as a hygroscopic foam;  $R_f$  0.20 in D, lit. 0.30 (2:1 CHCl<sub>3</sub>-MeOH) [9];  $[\alpha]_D^{20} - 4.4^\circ$ (c 0.8, H<sub>2</sub>O), lit. -4.0° [9]; NMR data corresponded to those previously published [9].

 $\beta$ -D-Fructofuranosyl 2,3-anhydro- $\alpha$ -D-mannopyranoside (13, 2, 3-anhydro-manno-sucrose).—Sucrose heptaacetate 3 (1.28 g, 2 mmol) was converted into the triflate 6 as described above, but without chromatographic purification. The resulting crude syrup was dissolved in 50 mL dry MeOH (molecular sieves 3 Å) under an atmosphere of  $N_2$ . Sodium methoxide (1.1 g, 20 mmol) was added and the mixture was stirred for 15 min at room temperature followed by neutralization with Amberlite IR-120 (H<sup>+</sup>-form). Filtration, concn of the filtrate under reduced pressure, elution of the residual syrup from a silica gel column  $(5 \times 20 \text{ cm})$  with 6:1 MeCN-water gave 483 mg of 13 (74%) based on 3 as a colorless syrup;  $R_f$  0.45 in D;  $[\alpha]_D^{20} + 35.5^\circ$  (c 1.0, MeOH); <sup>1</sup>H NMR (300 MHz,  $D_2O$ ):  $\delta$  3.29 (d, 1 H, H-2), 3.47 (d, 1 H,

H-3), 3.64–3.98 (m, 9 H, H-4, H-5, 2 H-6, 2 H-1', H-5', 2 H-6'), 4.09 (dd, 1 H, H-4'), 4.20 (d, 1 H, H-3'), 5.64 (s, 1 H, H-1);  $J_{1,2} = J_{3,4}$  0,  $J_{2,3}$  3.8,  $J_{3',4'}$ 8.7,  $J_{4',5'}$  8.6 Hz. <sup>13</sup>C NMR (75.5 MHz, D<sub>2</sub>O):  $\delta$ 53.4 (C-2), 58.4 (C-3), 63.2 (C-4), 63.8 (C-6), 64.3 (C-1'), 65.1 (C-6'), 73.0 (C-5), 76.6 (C-4'), 78.8 (C-3'), 84.2 (C-5'), 90.9 (C-1), 106.9 (C-2');  $J_{C-1,1-H}$ 170,  $J_{C-2,2-H}$  185,  $J_{C-3,3-H}$  183,  $J_{C-4,4-H}$  154,  $J_{C-5,5-H}$ 146,  $J_{C-6,6a-H}$  143,  $J_{C-6,6b-H}$  144,  $J_{C-1',1'a-H}$  142,  $J_{C-1',1'b-H}$  146,  $J_{C-3',3'-H}$  148,  $J_{C-4',4'-H}$  146,  $J_{C-5',5'-H}$ 149,  $J_{C-6',6'a-H}$  142,  $J_{C-6',6'b-H}$  145, hz. MS (FD, 15 mA): m/z 347, [MNa]<sup>+</sup>. Anal. Calcd for  $C_{12}H_{20}O_{10}$ : C, 44.40; H, 6.20. Found: C, 43.67; H, 6.40.

 $\beta$  - D - Fructofuranosyl 3 - amino - 3 - deoxy -  $\alpha$  - D altropyranoside (14, 3-amino-altro-sucrose).---A soln of epoxide 13 (340 mg, 1.05 mmol) was heated at 60 °C in ammonium hydroxide soln (25%) for 3 h. The reaction mixture was evaporated under reduced pressure to provide a residue which crystallized from MeOH in the form of colorless needles: 231 mg (64%) of **14**; mp 174 °C;  $[\alpha]_{D}^{20}$  +7.2° (*c* 1.2, H<sub>2</sub>O); <sup>1</sup>H NMR (300 MHz,  $D_2O$ ):  $\delta$  3.08 (dd, 1 H, H-3), 3.67 (m, 2 H, 2 H-1'), 3.71 (dd, 1 H, H-2), 3.81 (m, 4 H, 2 H-6, 2 H-6'), 3.89 (m, 1 H, H-5'), 3.95 (dd, 1 H, H-4), 4.01 (m, 1 H, H-5), 4.16 (dd, 1 H, H-4'), 4.21 (d, 1 H, H-3'), 5.17 (d, 1 H, H-1); J<sub>1,2</sub> 4.3, J<sub>2,3</sub> 6.5,  $J_{3,4}$  4.0,  $J_{4,5}$  6.8,  $J_{3',4'} = J_{4',5'}$  8.3 Hz. <sup>1.1</sup><sub>3</sub>C NMR (75.5 MHz, D<sub>2</sub>O): δ 52.9 (C-3), 60.6, 62.0 (C-6, C-6'), 61.5 (C-1'), 65.4 (C-4), 71.0 (C-2), 73.5 (C-5), 73.6 (C-4'), 76.4 (C-3'), 81.9 (C-5'), 93.8 (C-1), 104.5 (C-2'). MS (FD, 20 mA): m/z 342, [MH]<sup>+</sup>, 163, [fructofuranosyl]<sup>+</sup>, [3-amino-altropyranosyl + 1]<sup>+</sup>. Anal. Calcd for  $C_{12}H_{23}O_{10}N$ : C, 42.23; H, 6.79; N, 4.10. Found: C, 40.45; H, 6.46; N, 3.74.

 $\beta$ -D-Fructofuranosyl 3 - azido - 3 - deoxy - α - Daltropyranoside (15, 3-azido-altro-sucrose).—To a soln of 13 (170 mg, 0.52 mmol) in 90% EtOH (6 mL), NaN<sub>3</sub> (510 mg, 7.9 mmol) and NH<sub>4</sub>Cl (410 mg, 7.9 mmol) were added. After refluxing for 24 h the reaction mixture was filtered and the filtrate was evaporated under reduced pressure to provide crude 3-azide 15 (254 mg). Its  $R_f$  value (in D) was identical with that of 13, but distinguishable by a yellow– brown coloring on the TLC after heating; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ 5.19 (d, 1 H, H-1);  $J_{1,2}$  2.5 Hz. <sup>13</sup>C NMR (75.5 MHz, D<sub>2</sub>O): δ 62.6, 63.7, 64.5 (C-6, C-1', C-6'), 64.9, 68.0, 71.8, 76.1, 77.1, 78.8 (C-2, C-3, C-4, C-5, C-3', C-4'), 84.3 (C-5'), 95.9 (C-1), 106.83 (C-2').

 $\beta$ -D-Fructofuranosyl 3-acetamido-3-deoxy- $\alpha$ -Daltropyranoside (16, 3-acetamido-altro-sucrose).—A

soln of crude azide 15 (166 mg) in MeOH (15 mL), Ac<sub>2</sub>O (0.1 mL), and a catalytic amount of CH<sub>3</sub>COOH was hydrogenated over 10% Pd/C. After 24 h, the mixture was filtered, concd under reduced pressure, and purified by elution from a silica gel column  $(2 \times 22 \text{ cm})$  with 6:1 MeCN-water to afford 59 mg of syrupy 16 (45% based on 13);  $R_{f}$  0.22 in D; <sup>1</sup>H NMR (300 MHz,  $D_2O$ ):  $\delta$  2.05 (s, 3 H, Ac), 3.65 (dd, 2 H, 2 H-1'), 3.77 (dd, 1 H, H-2), 3.79-3.87 (m, 4 H, 2 H-6, 2 H-6'), 3.88-3.95 (m, 1 H, H-5'), 3.98 (m, 1 H, H-5), 4.01 (dd, 1 H, H-4), 4.17 (dd, 1 H, H-4'), 4.24 (d, 1 H, H-3'), 4.28 (dd, 1 H, H-3), 5.25 (d, 1 H, H-1);  $J_{1,2}$  3.6,  $J_{2,3}$  5.9,  $J_{3,4} = J_{4,5}$  4.2,  $J_{1'a,1'b}$  12.3,  $J_{3',4'}$  8.7,  $J_{4',5'}$  7.9 Hz. <sup>13</sup>C NMR (75.5 MHz, D<sub>2</sub>O): δ 25.0 (COMe), 54.2 (C-3), 63.1 (C-6), 63.7 (C-1'), 64.7 (C-6'), 66.3 (C-4), 71.6 (C-2), 75.5 (C-5), 76.3 (C-4'), 78.6 (C-3'), 84.6 (C-5'), 95.8 (C-1), 106.9 (C-2'), 177.2 (COMe).

 $\beta$ -D-Fructofuranosyl  $\alpha$ -D-altro-pyranoside (17, altro-sucrose).—A soln of epoxide 13 (176 mg, 0.54 mmol) in tri-distilled water was heated at 75 °C for 24 h. Concn and purification by elution from a silica gel column  $(2 \times 22 \text{ cm})$  with 10:1 MeCN-water afforded 38 mg (20%) of 17 as a colorless syrup;  $R_{\rm f}$ 0.06 in E;  $[\alpha]_{D}^{20} + 7.0^{\circ} (c \ 1.0, \ H_{2}O); \ ^{1}H \ NMR (800)$ MHz, D<sub>2</sub>O, 303 K): δ 3.80 (dd, 2 H, 2 H-1'), 3.91 (dd, 1 H, H-2), 3.94 (m, 4 H, 2 H-6, 2 H-6'), 4.02 (m, 2 H, H-3, H-5'), 4.05 (dd, 1 H, H-4), 4.19 (m, 1 H, H-5), 4.29 (dd, 1 H, H-4'), 4.31 (d, 1 H, H-3'), 5.31 (d, 1 H, H-1);  $J_{1,2}$  4.20,  $J_{2,3}$  6.30,  $J_{3,4}$  3.62,  $J_{4,5}$ 6.77,  $J_{1a',1b'}$  12.35,  $J_{3',4'}$  8.60,  $J_{4',5'} \approx 8.3$  Hz. <sup>13</sup>C NMR (75.5 MHz, D<sub>2</sub>O): δ 62.9 (C-6), 63.9 (C-1'), 64.5 (C-6'), 68.3 (C-4), 72.9 (C-3), 73.3 (C-2), 76.0 (C-5), 76.1 (C-4'), 79.0 (C-3'), 84.3 (C-5'), 96.2 (C-1), 107.0 (C-2'). MS (FD, 25 mA): m/z 365, [MNa]<sup>+</sup>, 163, [altropyranosyl]<sup>+</sup>, [fructofuranosyl]<sup>+</sup>.

1,3,4,6-Tetra-O-acetyl-β-D-fructofuranosyl 2,3,4,6tetra-O-acetyl-α-D-altropyranoside (**18**, altro-sucroseoctaacetate).—A soln of **17** (60 mg, 0.18 mmol) was acetylated using Ac<sub>2</sub>O (0.55 mL, 5.8 mmol) in 8 mL of pyridine. The crude product was purified by elution from a silica gel column (3 × 4.5 cm) with 1:1 toluene–EtOAc yielding 84 mg (71%) of **18** as a colorless syrup;  $R_f$  0.31 in C;  $[\alpha]_{D}^{20}$  – 3.8° (*c* 2.9, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.04–2.16 (8 s, 3 H each, 8 Ac), 4.16–4.37 (m, 7 H, 2 H-6, 2 H-1', H-5', 2 H-6'), 4.55 (m, 1 H, H-5), 4.89 (dd, 1 H, H-2), 5.17 (dd, 1 H, H-4), 5.27 (dd, 1 H, H-3), 5.34 (bs, 1 H, H-1), 5.44–5.50 (m, 2 H, H-3', H-4');  $J_{1,2}$  1.3,  $J_{2,3}$  3.6,  $J_{3,4}$  3.5,  $J_{4,5}$  10.0 Hz. <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  19.6–20.4 (CO*Me*), 61.4 (C-1'), 62.7 (C-6 and C-6'), 63.5 (C-4), 64.6 (C-5), 66.0 (C-3), 68.9 (C-2), 73.5, 74.8 (C-3', C-4'), 77.2 (C-5'), 90.3 (C-1), 102.3 (C-2'), 168.3-169.7 (COMe). MS (FD, 20 mA): m/z 678,  $[M]^+$ , 618,  $[M - MeCOOH]^+$ , 331, [tetraacetyl – fructofuranosyl]<sup>+</sup>. Anal. Calcd for C<sub>28</sub>H<sub>38</sub>O<sub>19</sub>: C, 49.56; H, 5.64. Found: C, 48.59; H, 6.01.

Sweetness evaluation.—To get a fairly reliable notion on the relative sweetness of the newly prepared sucrose isomers with manno- (8) and altroconfiguration (17) in the pyranoid portion, an ad hoc tasting team of five persons was established and pre-trained to evaluate sweetness over several consecutive days by tasting 1-5% solns of sucrose, fructose, and isomalt<sup>®</sup>, a low-calorie sugar substitute of Südzucker AG, comprising a 1:1 mixture of 1-O-( $\alpha$ -D-glucopyranosyl)-D-mannitol and 6-O-( $\alpha$ -D-glucopyranosyl)-D-glucitol. Thereby a small amount of the respective solns was placed on the tip of the tongue using plastic syringes; the panellists were asked to rinse their mouth with plain tapwater between the samples.

Thus prepared, the panellists evaluated a 5% soln of *manno*-sucrose (8) and *altro*-sucrose (17), as well as a 10% soln of 2-deoxy-sucrose [9] against 1 and 2% solns of sucrose. In full agreement of all panellists, 2-deoxy-sucrose was found to be about 10 times less sweet than sucrose, *manno*-sucrose to be about 5 times less sweet (i.e. distinctly sweeter than 2deoxy-sucrose, 80% agreement of panellists), whereas *altro*-sucrose in the concn used (5%) was devoid of sensible sweetness.

### Acknowledgements

The <sup>1</sup>H 800-MHz spectra of *altro*-sucrose (17) were recorded at the Large Scale Facility for Biomolecular NMR in Frankfurt; we are most grateful to Prof. Dr. C. Griesinger and Dr. H. Schwalbe for support. The authors also express their appreciation to the Bundesministerium für Ernährung, Landwirtschaft und Forsten, Bonn (project number 93 NR144-F), and the Südzucker AG, Mannheim/ Ochsenfurt for financial support.

#### References

- [1] A. Hugill, Introductory Dedicational Metaphor, in Sugar and all That. A History of Tate and Lyle, Gentry Books, London, 1978.
- [2] C.E. James, L. Hough, and R. Khan, Prog. Chem. Org. Nat. Prod., 55 (1989) 117–184.

- [3] S. Abouhilale, J. Greiner, and J.G. Riess, *Carbohydr. Res.*, 212 (1991) 55–64.
- [4] C. Chauvin and D. Plusquellec, *Tetrahedron Lett.*, 32 (1991) 3495–3498.
- [5] T. Otake, Bull. Chem. Soc. Jpn., 43 (1970) 3199– 3205.
- [6] H. Carl and C.K. Lee, *Carbohydr. Res.*, 101 (1982) 31–38.
- [7] W. Moody, G.N. Richards, N.W.H. Cheetham, and P. Sirimanne, *Carbohydr. Res.*, 114 (1983) 306–310.
- [8] C. Chauvin, K. Baczko, and D. Plusquellec, J. Org. Chem., 58 (1993) 2291–2295.
- [9] F.W. Lichtenthaler, S. Immel, and P. Pokinskyj, Liebigs Ann. Chem., (1995) 1939–1947.
- [10] K. Sato and A. Yoshitomo, *Chem. Lett.*, (1995) 39–40.
- [11] Y. Nogami, K. Nasu, T. Koga, K. Ohta, K. Fujita, S. Immel, H.J. Lindner, G.E. Schmitt, and F.W. Lichtenthaler, Angew. Chem., 109 (1997) in press; Angew. Chem. Int. Ed. Engl., 35 (1997) in press.
- [12] F. Sweet and R.K. Brown, Can. J. Chem., 46 (1968) 1481–1486.
- [13] D.H. Buss, L. Hough, L.D. Hall, and J.F. Manville, *Tetrahedron*, 21 (1965) 69-74.
- [14] J.G. Buchanan, J.C.P. Schwarz, K. Parry, and W.A. Thomas, J. Chem. Soc., (1962) 4770–4777.
- [15] J.G. Buchanan and D.M. Clode, J. Chem. Soc., Perkin Trans. 1, (1974) 388–394.

- [16] J.G. Buchanan and R. Fletcher, J. Chem. Soc. B, (1969) 377-385.
- [17] S.J. Angyal, Aust. J. Chem., 21 (1968) 2737–2746;
  S.J. Angyal and V.A. Pickles, Aust. J. Chem., 25 (1972) 1695–1710.
- [18] K. Fujita, H. Shimada, K. Ohta, Y. Nogami, K. Nasu, and T. Koga, Angew. Chem., 107 (1995) 1783–1784; Angew. Chem. Int. Ed. Engl., 34 (1995) 1621–1622.
- [19] K. Fujita, K. Ohta, Y. Ikegami, H. Shimada, T. Tahara, Y. Nogami, T. Koga, K. Saito, and T. Nakajima, *Tetrahedron Lett.*, 35 (1994) 9577–9580.
- [20] T. Murakami, K. Harata, and S. Morimoto, Chem. Lett., (1988) 553-556.
- [21] K. Fujita, Y. Egashira, T. Imoto, T. Fujioka, K. Mihashi, T. Tahara, and T. Koga, *Chem. Lett.*, (1989) 429–432.
- [22] R. Breslow and A.W. Czarnik, J. Am. Chem. Soc., 105 (1983) 1390–1391.
- [23] B. Coxon, Carbohydr. Res., 1 (1966) 357-364.
- [24] F.W. Lichtenthaler, S. Immel, D. Martin, and V. Müller, *Starch / Stärke*, 44 (1992) 445–456.
- [25] F.W. Lichtenthaler and S. Immel, in M. Mathlouthi, J.A. Kanters, and G.G. Birch (Eds.), Sweet Taste Chemoreception, Elsevier Applied Science, London/New York, 1993, pp 21-53.
- [26] F.W. Lichtenthaler and S. Immel, Int. Sugar J., 97 (1995) 12–22.