Molecular Modeling of Saccharides, 8[◇]

Selective 2-*O*-Benzylation of Sucrose: A Facile Entry to Its 2-Deoxy- and 2-Keto-Derivatives and to Sucrosamine

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Received June 2, 1995

Key Words: Sucrose / Molecular electrostatic potential (MEP) / 2-*O*-Modified derivatives / Monobenzylation, selective

Generation of the molecular electrostatic potential (MEP) profiles, in color-coded form, on the solvent-accessible contact surfaces of the two main conformations that sucrose adopts in vacuo as well as in aprotic solvents (e.g. DMF), clearly shows the secondary glucosyl-2-OH to be the most electropositive of the altogether eight hydroxyl groups – conceivably due to the persistence of an intramolecular hydrogen bond of the 2^g-O···HO-1^f type. The notion that the 2^g-OH is accordingly the hydroxyl group most readily deprotonated in aprotic solvents, and that the resulting sucrose 2^g-*O*-alkoxide is the one best stabilized by intramolecular hydrogen bonding, received ample substantiation by smoothly achieving a highly regioselective (>80%) 2^g-*O*-benzylation in DMF with NaH/benzyl bromide. The resulting 2^g-*O*-benzyl-sucrose (**2**) – minor products being the 1^f-*O*- (**3**) and 3^f-*O*-isomers (**4**) – was converted, by acetylation and hydrogenolysis into the 2^g-OH-free sucrose heptaacetate **6**, isolable in crystalline form in 42% yield based on sucrose, thus opening up a ready entry to 2^g-*O*-modified derivatives: 2-deoxy-sucrose (**12**) via radical deoxygenation of a 2^g-*O*-thiocarbamate, 2-keto-sucrose perbenzoate **7** via PDC oxidation, or *N*-acetyl-sucrosamine **14** and its *manno*-analog **16** through oximation of **7** and subsequent borane reduction.

Sucrose occupies a key position amongst the readily accessible disaccharides, such that it has affectionately been designated the "royal carbohydrate"[2]. With an annual production of over a 100 million tons it clearly is the world's most abundantly produced organic compound, and this in unparalleled purity. Although its chemistry is fairly well developed[3–5], still by far the major portion of the total production is utilized as a sweetener of processed or directly consumed foods; less than 5% is directed to non-food uses.

The reasons for this lie in the chemical limitations imposed by the instability of the glycosidic 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, such that regioselective functionalizations are difficult to achieve. Thus, the accessibility of any given sucrose derivative depends on the efficiency with which a selective *mono*-functionalization can be effected, either directly, or by chemically blocking seven of the eight hydroxyl groups leaving one free for further manipulation.

There are various procedures in the literature for chemically[4,6–8] or enzymatically[9] effecting *mono-O-acylations*, yet the most readily accessible derivatives are those carrying the acyl function at the primary hydroxyl groups, i.e. at the 6^g-*O*-, 6^f-*O*-, and/or 1^f-*O*-positions[*] – a type of mono-functionalization that is of little use for performing chemical modifications at the pyranoid or furanoid ring carbons of sucrose. Only when special heterocyclic acylation agents are used, have reasonably high mono-acylations at the glucosyl-2-OH been obtained[8].

Selective *mono-O-alkylations* of sucrose appear even more difficult to achieve[4]. Tritylation and silylation with *t*-butyldimethylsilyl or *t*-butyldiphenylsilyl chloride preferentially seizes the primary hydroxyl groups in the order 6^g-OH, 6^f-OH, and 1^f-OH[*]. Yet their differentiation in preparative terms are modest: the 6^g-*O*- and 6^f-*O*-trityl-sucroses may be obtained in about 20% each[10], the 6^f-*O*-*t*-butyldiphenyl ether in 49%[11]. Methylation of sucrose proceeds with lesser regioselectivity, requiring extensive chromatography for the acquisition of pure mono-methyl ethers, the 3^f-*O*- and 4^g-*O*-methyl derivatives being major products under carefully controlled conditions (dimethyl sulfate/sodium hydroxide)[12]. An early study of the benzylation of sucrose, performed in DMF solution with benzyl bromide in the presence of silver oxide, revealed a surprisingly high preference for the glucosyl-2-OH: an 86:10:3:1 mixture of four mono-benzyl ethers was obtained in 40% yield, with the 2^g-*O*- and 3^f-*O*-benzyl derivatives as the major products[13]. The electrolysis of sucrose in DMF and subsequent quenching of the mono-anion generated with benzyl bro-

[◇] Part 7: Ref.[1].

[*] For more ready differentiation of the oxygens in the fructose (primed numbers usually) and the glucose portions, they are denoted with "f" and "g" superscripts, respectively.

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mide, exhibited a lower selectivity though as a 4:3:1 mixture of mono-benzyl-sucroses accumulated, the 2^g-*O*-benzyl derivative being one of the main components[14].

Because electrolytic generation of the mono-alkoxide of sucrose is preparatively impractical due to the high salt concentration in the reaction medium, and because of the necessity for batchwise operation and for cessation at 40–50% consumption of the substrate[14], only the chemical deprotonation has the potential – if adaptable to bases other than silver oxide – to provide an entry into hitherto quite elusive 2-derivatized sucroses. The 2-keto-sucrose, for example, has been obtained only as part of a mixture resulting from bromine oxidation of sucrose[15], the 2-amino analog of sucrose ("sucrosamine") has been prepared rather laboriously by fructosylation of glucosamine[16], and 2-deoxy-sucrose was obtained enzymatically in small amounts[17] and chemically via an as yet undisclosed route[18].

Encouraged by computer generation of the molecular electrostatic potential (MEP) profiles of the major sucrose conformers[19,20] to be detailed herein, as well as the synthetic potential of a selective 2^g-*O*-benzylation of sucrose, we have reinvestigated this reaction[20], and report the results on the straightforward preparation of 2-keto, 2-deoxy and 2-acetamido derivatives of sucrose.

1. The Molecular Electrostatic Potential (MEP) Profile of Sucrose

A detailed molecular mechanics and dynamics analysis of the conformational properties of sucrose revealed, for polar aprotic solvents the presence of two relevant conformers[1] that differ in the orientation of the glucose and fructose portions relative to each other. The major conformer S1 is characterized by a 2^g-O···HO-1^f interresidue hydrogen bond, while the minor structure exhibits an alternative 2^g-O···HO-3^f hydrogen bonding interaction. In the preceding report[1] we have detailed the force-field based geometry analysis, including the generation of molecular contact surfaces[21] that properly describe the steric demands of both sucrose conformers. Aside purely sterical factors, the distribution of electrophilic and/or nucleophilic sites over these solvent-accessible-surfaces of the sucrose molecules is a decisive element in assessing its reactivity and the regioselectivities attainable in reactions. Thus, it is of vital importance, to know about the distribution of the charge density or electrostatic potential over the surface of the two conformers[1].

Generation of the molecular electrostatic potential (MEP)[22,23] profiles for the sucrose conformers S1 and S2 can be effected by classical electrostatic laws, namely

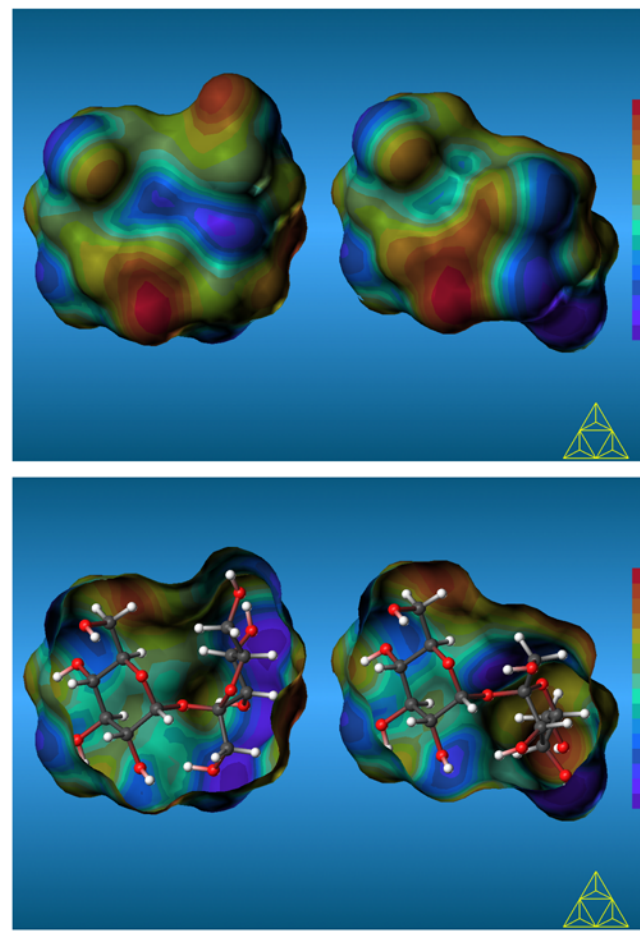
$$\mathrm{MEP}\,(\vec{r}) = \sum_{i=1}^{n} q_i/|\vec{r} - \vec{r}_i|$$

where n is the number of atoms in the molecule and r_i is the position vector for the i-th atom, starting from atomic partial charges q_i, which may be calculated by different methods including semiempirical or *ab initio* approaches. As there is no unique way to determine the effective partial atomic charges from the electronic charge distribution, here the AM1[24]-atomic charges were used, computed with the MOPAC-program package[25].

The MEP values calculated for each of the two sucrose conformers S1 and S2, are transferred into a 16-color code ranging from red for the most electropositive area to violet for the region(s) of highest electronegative potential[26], and are visualized with the MOLCAD program[27] by using texture mapping strategies[28].

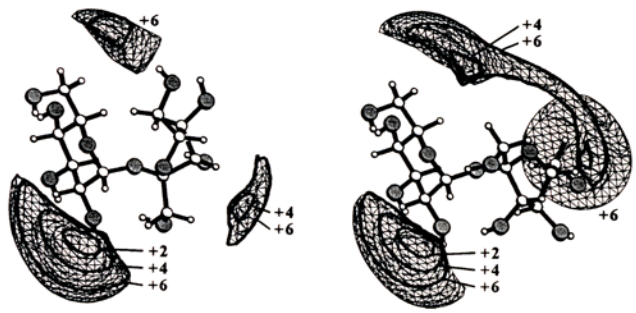
The resulting MEP patterns for each of the two relevant sucrose conformers are given in Figure 1. As is clearly evident, the area of the 2^g-OH group of the glucose portion, that is, the most intense red surface part, is the one with the highest positive electrostatic potential. This is undoubtedly caused by the cooperativity[29] of the hydrogen bond directed towards the oxygen of this hydroxyl group. The electron-withdrawing effect of the adjacent anomeric center can contribute only to a minor extent, since it would have to effect the 1^f- and 3^f-OH groups in the fructose moiety in the same way.

Figure 1. Representation of the molecular electrostatic potential (MEP) profiles of sucrose conformers S1 (left) and S2 (right) on the corresponding contact surfaces[1] in a 16-color code ranging from violet (most negative potential) to red (most electropositive potential) in relative terms. To facilitate visualization, the front side-opened forms of the two conformers are also provided with a ball-and-stick model inserted in either case. It is evident that the glucosyl-2-OH proton is characterized by the most positive electrostatic potential (red)



The strong positivation of the 2^g-OH group becomes particularly evident when calculating iso-energy contour surfaces[27] for the interaction of a negatively charged probe sphere with the sucrose molecule. At negative energy levels, these iso-energy plots delineate spatial volumes of energetically favorable interactions with a nucleophile. In Figure 2, the energy contours for sucrose conformers S1 and S2 are given at levels of +2, +4, and +6 kcal/mol above the respective global energy minimum of about −10.5 kcal/mol. In either case, the lowest energy and thus most electrophilic regions are invariably centered around the glucosyl-2-OH-group.

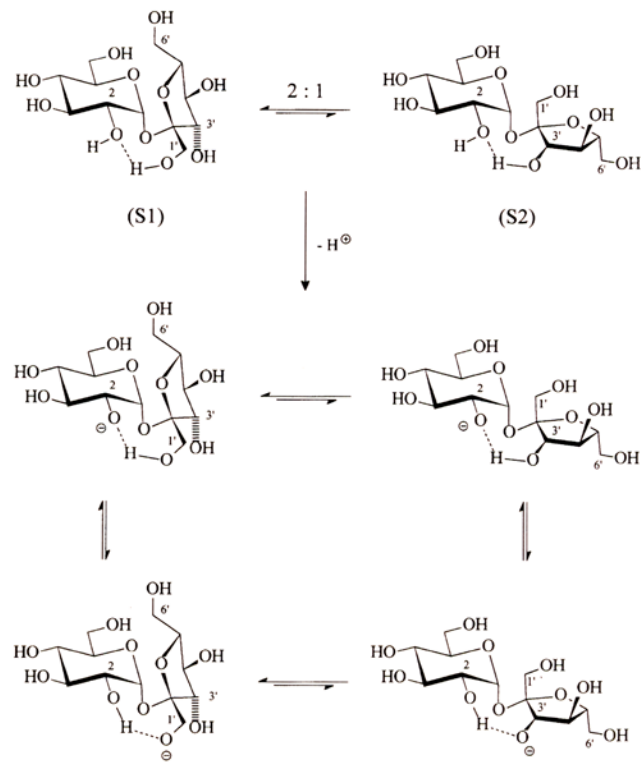
Figure 2. Iso-energy contour plots for the interactions of a negatively charged probe sphere with the two sucrose conformers S1 and S2. Contours are drawn at levels of +2, +4, and +6 kcal/mol above the respective global energy minimum. The high positivation of the glucosyl-2-OH points towards an enhanced acidity of this hydroxyl group over the others, as well as to its energetically favorable hydrogen bond donor capabilities



The pronounced positivation around the 2^g-OH necessarily suggests, that the acidity of this hydroxyl group is higher than those of the other seven, that is, it should be deprotonated first on base treatment. There is some experimental evidence that this indeed is the fact. It has been demonstrated[8] that the 2^g-*O*-acyl and 2^g-*O*-(*N*-carbamoyl)-derivatives of sucrose are obtained in useful yields by NaH-deprotonation of sucrose in pyridine and reaction with mild heterocyclic acylating agents such as 3-acyl-thiazolidinethiones. The high preference for the formation of 2^g-*O*-benzyl-sucrose on silver oxide-promoted benzylation in DMF[13] obviously yields to a similar explanation. Similarly, the selectivities obtained by electroreductive deprotonation of sucrose within the cathodic compartment of an electrolysis cell, followed by trapping with alkylating agents[14], can be rationalized on the basis of the MEP profiles of Figure 1: The sucrose molecule is oriented in the electric field in such a way that the glucosyl-2-OH side is directed towards, and hence arrives at the cathode eliciting the single electron transfer (SET) at that very position by which the 2^g-OH is converted into the alkoxide. Although we favor this possibility, there is an alternative: SET-induced deprotonation occurs at another hydroxyl group of sucrose, for example, at one of the sterically more accessible primary hydroxyls (6^g-OH, 1^f-OH of 6^f-OH), and the resulting mono-alkoxide undergoes fast equilibration via intra- or inter-molecular proton shifts between the various OH-groups, thus creating the thermodynamically most stable anion. The time scales for the formation of the radical anion, for releasing a hydrogen atom, equilibration, and the subsequent trapping reactions of the anions (even when carried out *in situ*) differ by several orders of magnitude, and therefore, the observed product distribution upon trapping the anions by alkylation or acylation may be the result of the regioselectivity in the electrochemically induced deprotonation step, but this must not necessarily be so.

Irrespective of the actual site of deprotonation – be it directly at the glucosyl-2-OH, or elsewhere and followed by intramolecular proton shifts – the thermodynamically most stable sucrose mono-alkoxide appears to receive its stabilization by intramolecular hydrogen bonding between the 1^f-OH and 2^g-O, and, to a lesser extent, between the 3^f-OH and the 2^g-O, as indicated in the formulae of Figure 3.

Figure 3. Sucrose in an aprotic, polar solvent (DMF or DMSO), for which a 2:1 equilibrium distribution of conformers S1 and S2 has been suggested on the basis of SIMPLE ^{1}H NMR measurements[30], and its mono-alkoxide resulting from NaH-deprotonation in DMF



Assuming, that the equilibrium between the two sucrose conformers S1 and S2 (as depicted in Figure 1), – in DMSO solution a 2:1 ratio has been determined by SIMPLE ^{1}H NMR[30] – is the same, or at least very similar for the mono-alkoxide, chemical trapping by suitable reagents should give the 2^g-*O*-, 1^f-*O*- and 3^f-*O*-substituted products in that order of preference. These MEP-derived rationalizations and their correlation with some experimental findings[8,13,14] prompted us to reinvestigate the benzylation of sucrose for exploitation towards C-2 modified derivatives.

2. Benzylation of Sucrose

For the deprotonation of sucrose, sodium hydride was considered to be more practical than the use of silver oxide[13]. Accordingly, exposure of a DMF solution of sucrose to 0.9 equivalents of NaH for 1 h at 0°C, followed by addition of benzyl bromide resulted in an 11:2:1 mixture of three monobenzyl ethers in which the 2^g-*O*-benzyl-sucrose (**2**) was the major product (>80% based on ^{1}H NMR). The reaction proceeded only 70%, yet was not forced any further to keep introduction of more than one benzyl group at a minimum. While removal of the unreacted sucrose was simple, the separation of the three mono benzyl ethers, namely, **2** and its 1^f-*O*- (**3**) and 3^f-*O*-benzyl isomers (**4**) by various chromatographic means proved to be exceedingly difficult, and hence, was only carried out on an analytical scale for characterizing the benzylation sites unequivocally. The mixture was peracetylated and subjected to repeated chromatography on silica gel to provide the syrupy heptaacetates of **2** (in pure form), **3** and **4** (of about 90% purity), which as such, or after Zemplén de-*O*-acetylation to **2**, **3**, and **4**, respectively, were submitted to NMR measurements. While the ^{1}H NMR data of **2**, **3**, and **4** gave only small chemical shift differences for the CH or CH_2 carrying the benzyloxy group, the chemical shifts of the ^{13}C resonances (cf. Table 1) show a distinct downfield shift of about 6–8 ppm for the carbons with benzylated oxygens. This clear-cut shift pattern unambiguously established the benzylation sites of the minor products to be in the fructose portion, at 1^f-*O* (**3**) and 3^f-*O* (**4**), respectively, as well as that of the main component, 2^g-*O*-benzyl-sucrose (**2**), for which structural evidence was even more convincingly derived from its ensuing products.

In terms of the utilization of **2** for preparative purposes, it proved advantageous not to separate the crude mixture of mono-benzyl-ethers obtained at the acylated stage, but one step further, that is, after hydrogenolysis of the benzyl ether groups. The 2^g-OH-free hepta-*O*-acetyl-sucrose (**6**) crystallized exceedingly well, and in this way could be readily secured in pure form. The yield of 42% for the three steps from sucrose was quite satisfactory.

Ready access to the 2^g-OH-free sucrose-heptaacetate **6** being thus accomplished, ensuing reactions were studied. Thiocarbonylation of **6** with thiocarbonyldiimidazole and subsequent reduction by tributyltin hydride in toluene according to standard procedures[31] smoothly generated the heptaacetate **11**, which upon deacetylation provided the 2-deoxysucrose (**12**) in the useful overall yield of 63% for the three step-sequence from **6**.

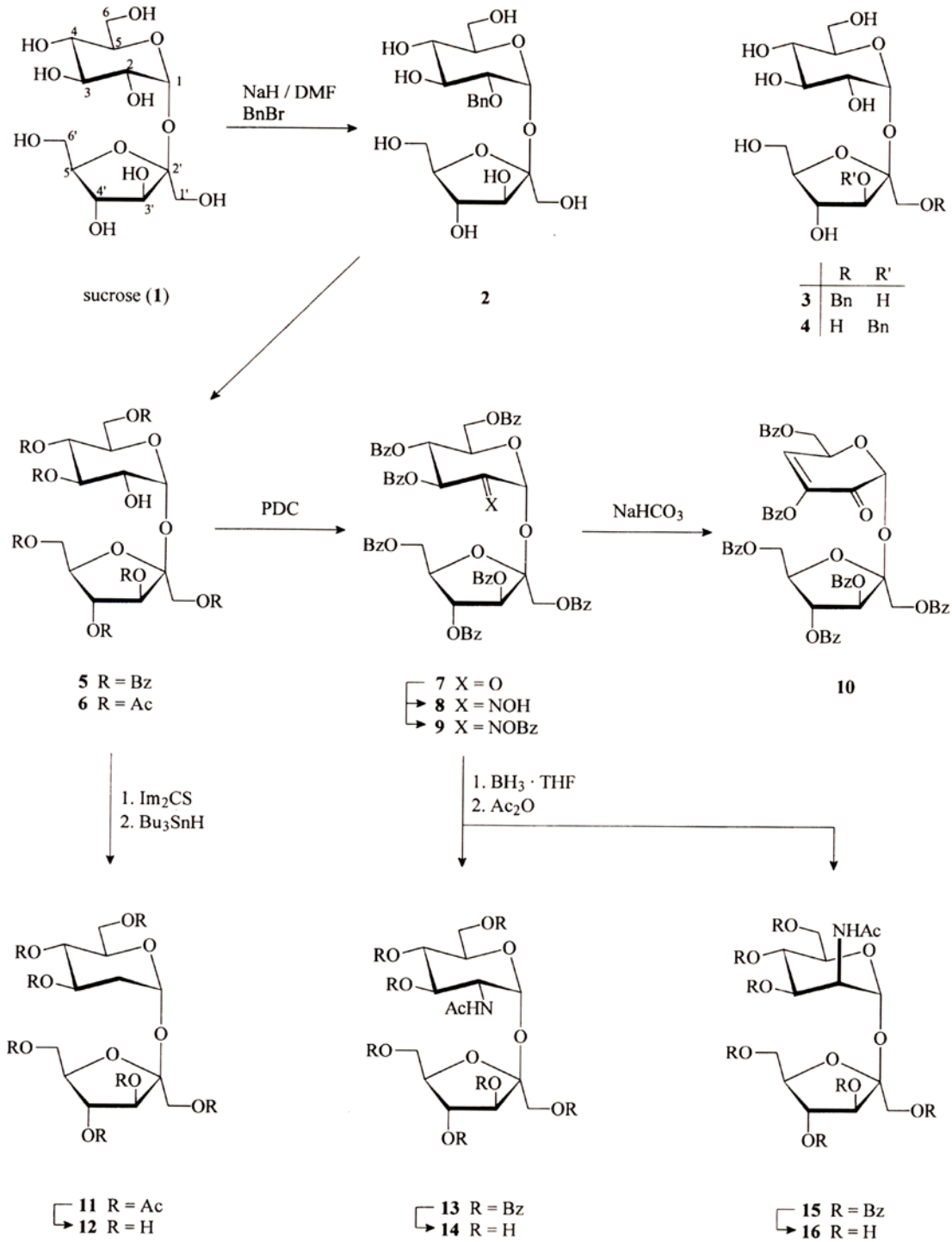
Oxidation of heptaacetate **6** with pyridinium dichromate (PDC) gave a mixture of several products, obviously due to the propensity of the 2-keto-heptaacetate for β-elimination. The corresponding 2^g-OH-free heptabenzoate **5**, however, prepared by benzoylation of the crude mixture of monobenzyl ethers smoothly afforded the respective 2-keto-sucrose derivative **7** when exposed to PDC oxidation. Slightly basic conditions, such as stirring in acetonitrile with solid sodium hydrogen carbonate, not unexpectedly[32], induced quantitative elimination of benzoic acid from the 3,4-positions to yield **10**, a fructosylated dihydropyranone, and as such a versatile enantiopure building block.

The 2-keto-sucrose heptabenzoate **7** also proved to be a suitable starting material for the generation of 2-amino derivatives of sucrose. Oximation (→**8**) and benzoylation gave the *O*-benzoyloxime **9** which on $BH_3 \cdot THF$ reduction proceeded with an approximate 2:1 stereoselectivity for hydride addition from the β-side. *N*-Acetylation provided the respective heptabenzoates of *N*-acetylsucrosamine (**13**) and its mannosamine-analog **15** in isolable yields of 48 and 29%, respectively. Both could be smoothly deblocked under Zemplén conditions to the respective *N*-acetates **14** and **16**, that were unequivocally characterized on the basis of their NMR data. In the case of *N*-acetylsucrosamine **14**, the spectral data correlated well with those for a product, prepared by fructosylation of glucosamine[16]; yet the larger rotational value found by us (+84° in water vs. +71°[16]) indicated higher purity.

This work was supported by the *Bundesministerium für Forschung und Technik* (BMFT grant 0319251A), the *Südzucker AG*, Mannheim-Ochsenfurt, and the *Fonds der Chemischen Industrie*, Frankfurt am Main, to whom our thanks are due. We are also most grateful to Prof. Dr. *J. Brickmann*, Institut für Physikalische Chemie of this University, for generously providing as the MOLCAD modeling software package[27] and his sophisticated computational facilities.

Table 1. ^{13}C-NMR shifts of the mono-*O*-benzyl sucroses **2**–**4** in D_2O and their heptaacetates in $CDCl_3$, revealing the sites of *O*-benzylation through a 6–8 ppm downfield shift of the respective carbon, as indicated

		^{13}C NMR data											
		Glucose residue						Fructose residue					
		C-1	C-2	C-3	C-4	C-5	C-6	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'
benzyl-sucrose	**2**	93.1	**81.8**	75.1	72.3	75.0	63.0	64.2	106.7	79.0	76.8	84.2	65.2
	3	95.3	73.9	75.4	72.0	75.2	62.9	**71.5**	106.2	79.4	76.5	84.1	65.0
	4	94.8	73.9	75.6	72.0	75.1	62.9	65.4	106.7	**85.8**	76.4	84.2	65.0
peracetate of	**2**	90.2	**75.8**	71.7	68.3	68.5	61.9	63.4	103.5	75.3	74.5	78.7	63.3
	3	89.6	70.2	69.8	68.3	68.2	61.7	**69.9**	104.5	75.7	74.7	78.5	63.5
	4	89.6	70.1	70.2	68.4	68.1	62.0	64.1	103.5	**81.0**	75.6	78.4	64.2



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. – TLC on silica gel 60 F_{254} plastic sheets (Merck, Darmstadt) was used to monitor the reactions and ascertain the purity of the products. Eluants employed: A = $CHCl_3$/MeOH (2:1), B = toluene/EtOAc (15:1), C = toluene/EtOAc (1:1), D = EtOAc/toluene (5:2), E = toluene/EtOAc (5:1), F = toluene/EtOAc (10:1), G = toluene/EtOAc (2:1). The spots were visualized by UV light or by spraying with 50% sulfuric acid and charring at 120°C for 5 min. Column chromatography was performed on silica gel 60 (Macherey & Nagel, 63–200 nm).

Monobenzylation of Sucrose (**1**): A suspension of 5.13 g (15 mmol) of **1** in 100 ml of DMF was heated to 80°C with exclusion of moisture (N_2-atmosphere, molecular sieve 4 Å) until a clear solution was obtained. The solution was then cooled to 0°C followed by the addition of 330 mg (13 mmol) of the commercially available 95% sodium hydride (or the equivalent of NaH in mineral oil). After stirring for 1 h, benzyl bromide (1.3 ml, 12 mmol) was added

and stirring at 0°C was continued for another 8 h. After evaporation of the solvent, starting material and higher benzylated sucrose derivatives were removed by elution from a silica gel column (4 × 35 cm) with $CHCl_3$/MeOH (2:1). Concentration of the fraction containing the monobenzyl ethers (R_f = 0.44 in A) gave 4.46 g (69% based on **1**, 86% based on benzyl bromide) of a syrup, consisting (GC after permethylation, cf. below) of an approximate 11:2:1 mixture of the 2-*O*-benzyl (**2**), 1′-*O*-benzyl (**3**), and 3′-*O*-benzyl (**4**) derivatives of sucrose.

This mixture was used for the ensuing experiments leading to heptabenzoate **5** and heptaacetate **6** via acylation and hydrogenolytic de-*O*-benzylation (cf. below).

The 11:2:1 ratio with which the mono-benzyl-sucroses **2**–**4** accumulate, was determined after permethylation (KOH/MeI) via GC-MS, using a HT-S fused silica capillary column and helium for separation and a Finnigan ITD 800 equipped with trap detector; isobutylamine as the reactant gas used for chemical ionization invariably gave the expected mass spectra with a base peak at *m/z* = 604 ($M^+ + i$BuNH$_2$).

For proof of the benzylation sites of **2**–**4**, a 900 mg portion of this mixture was acetylated and the peracetate mixture was subjected to repeated column chromatography on silica gel, eluting with toluene/EtOAc (2:1). The TLC mobilities of the three peracetates being very similar, the fractions obtained had to be inspected by ^{1}H NMR, revealing that the 1′-*O*-benzyl derivative (peracetate of **3**) was eluted somewhat faster from the main product (peracetate of **2**), while the 3′-*O*-benzyl isomer had the lowest mobility. Accordingly, after rechromatography of the first eluates, the two minor components had accumulated in the fractions eluted first and last respectively to the extent of 85–90%, while the major product, the heptaacetate of **2**, was obtained in pure form.

Hepta-O-acetyl-2-O-benzylsucrose (Heptaacetate of **2**): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01–2.13 (7 s, 3H each, 7 CH_3 of Ac), 3.57 (dd, 1H, 2-H), 4.02–4.36 (m, 8H, 5-H, 6-H, 1′-H$_2$, 5′-H, 6′-H$_2$), 4.51 and 4.64 (2 d, 1H each, CH_2C$_6$H$_5$), 4.97 (dd, 1H, 4-H), 5.38 (dd, 1H, 3-H), 5.44 (dd, 1H, 4′-H), 5.52 (d, 1H, 3′-H), 5.53 (d, 1H, 1-H), 7.39–7.95 (m, 5H, C$_6$H$_5$); $J_{1,2}$ = 3.6, $J_{2,3}$ = 9.8, $J_{3,4}$ = 9.7, $J_{3',4'}$ = $J_{4',5'}$ = 6.6 Hz. – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 61.9 (C-6), 63.3 (C-6′), 63.4 (C-1′), 68.3 (C-4′), 68.5 (C-5), 71.7 (C-3), 72.7 (CH_2C$_6$H$_5$), 74.5 (C-4′), 75.3 (C-3′), 75.7 (C-2), 78.7 (C-5′), 90.2 (C-1), 103.5 (C-2′), 127.8–137.3 (C$_6$H$_5$), 169.8–170.7 (CO of Ac). – MS (FD): *m/z* = 726 (M^+).

Hepta-O-acetyl-1′-O-benzylsucrose (Heptaacetate of **3**): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94–2.15 (m, 21H, 7 CH_3 of Ac), 3.41 (d, 1H, 1′-H$_a$), 3.60 (d, 1H, 1′-H$_b$), 4.11–4.23 (m, 3H, 5′-H, 6-H$_2$), 4.25–4.36 (m, 3H, 5-H, 6′-H$_2$), 4.59 (s, 2H, CH_2C$_6$H$_5$), 4.85 (dd, 1H, 2-H), 5.07 (dd, 1H, 4-H), 5.40 (dd, 1H, 4′-H), 5.43 (dd, 1H, 3-H), 5.67 (d, 1H, 1-H), 5.70 (d, 1H, 3′-H), 7.15–7.35 (m, 5H, C$_6$H$_5$); $J_{1,2}$ = 3.8, $J_{2,3}$ = 10.3, $J_{3,4}$ = 9.8, $J_{4,5}$ = 9.7, $J_{3',4'}$ = $J_{4',5'}$ = 6.8 Hz. – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.4–20.6 (CH_3 of Ac), 61.7 (C-6), 63.5 (C-6′), 68.2 (C-5), 68.3 (C-4), 69.8 (C-3), 69.9 (C-1′), 70.2 (C-2), 73.7 (CH_2C$_6$H$_5$), 74.7 (C-4′), 75.7 (C-3′), 78.5 (C-5′), 89.6 (C-1), 104.5 (C-2′), 127.7–129.0 (C$_6$H$_5$), 169.5–170.6 (CO).

Hepta-O-acetyl-3′-O-benzylsucrose (Heptaacetate of **4**): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98–2.13 (m, 21H, CH_3 of Ac), 3.95 (d, 1H, 1′-H$_a$), 4.06 (d, 1H, 1′-H$_b$), 4.02–4.16 (m, 3H, 5′-H, 6′-H$_2$), 4.20 (d, 1H, 3′-H), 4.27–4.39 (m, 3H, 5-H, 6-H$_2$), 4.62 (s, 2H, CH_2C$_6$H$_5$), 4.93 (dd, 1H, 2-H), 5.04 (dd, 1H, 4-H), 5.43 (dd, 1H, 4′-H), 5.51 (dd, 1H, 3-H), 5.73 (d, 1H, 1-H), 7.27–7.40 (m, 5H, C$_6$H$_5$); $J_{1,2}$ = 3.8, $J_{2,3}$ = 10.4, $J_{3,4}$ = 9.9, $J_{4,5}$ = 9.8, $J_{3',4'}$ = $J_{4',5'}$ = 7.4 Hz. – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8–20.9 (CH_3 of Ac), 62.0 (C-6), 64.1 (C-1′), 64.2 (C-6′), 68.1 (C-5), 68.4 (C-4), 70.1 (C-2), 70.2 (C-3), 73.2 (CH_2C$_6$H$_5$), 75.6 (C-4′), 78.4 (C-5′), 81.0 (C-3′), 89.6 (C-1), 103.5 (C-2′), 128.2–128.7 (C$_6$H$_5$), 169.7–170.9 (CO).

Small samples of each of the heptaacetates, as obtained above, were deacetylated by brief exposure to sodium methoxide/methanol and, upon standard work up, subjected to NMR spectroscopy, using 2D techniques for securing signal assignments; relevant ^{13}C resonances are listed in Table 1.

2-O-Benzylsucrose (**2**): ^{1}H NMR (300 MHz, D_2O): δ = 3.47 (d, 1H, 1′-H$_a$), 3.53 (m, 3H, 1′-H$_b$), 5-H, 5′-H), 3.75–3.90 (m, 7H, 2-H, 3-H, 4-H, 6-H$_2$, 6′-H$_2$), 4.03 (dd, 1-H$_2$, 4′-H), 4.19 (d, 1H, 3′-H), 4.76 (s, 2H, CH_2 of Bn), 5.53 (d, 1H, 1-H), 7.41–7.51 (m, 5H, C$_6$H$_5$); $J_{1,2}$ = 3.7, $J_{1',1'}$ = 9.5, $J_{3',4'}$ = 8.7, $J_{4',5'}$ = 8.5 Hz. – ^{13}C NMR (75.5 MHz, D_2O): δ = 60.5 (C-6′), 61.6 (C-1′), 62.7 (C-6), 69.7 (C-5), 72.5 (C-3), 72.6 (C-4), 74.2, 74.3 (C-4′, $CH_2C_6H_5$), 76.5 (C-3′), 79.3 (C-5′), 81.7 (C-2), 90.6 (C-1), 104.2 (C-2′), 128.9–129.4 (C$_6$H$_5$). – MS (FD): *m/z* = 466 (MNa^+), 433 (MH^+).

1′-O-Benzylsucrose (**3**): ^{1}H NMR (300 MHz, D_2O): δ = 3.49 (dd, 1H, 4-H), 3.51 (dd, 1H, 2-H), 3.63–3.89 (m, 8H, 1′-H$_2$, 6-H$_2$, 6′-H$_2$, 5′-H, 5-H), 3.74 (dd, 1H, 3-H), 4.06 (dd, 1H, 4′-H), 4.24 (d, 1H, 3′-H), 4.62 and 4.68 (two 11.7 Hz d, 1H each, CH_2 of Bn), 5.39 (d, 1H, 1-H), 7.42–7.46 (m, 5H, C$_6$H$_5$); $J_{1,2}$ = 3.8, $J_{2,3}$ = 9.4, $J_{3,4}$ = 9.5, $J_{3',4'}$ = $J_{4',5'}$ = 8.5 Hz. – ^{13}C NMR (75.5 MHz, D_2O): δ = 62.9 (C-6), 65.0 (C-6′), 71.5 (C-1′), 72.0 (C-4), 73.9 (C-2), 75.2 (C-5), 75.4 (C-3), 76.3 (CH_2C$_6$H$_5$), 76.5 (C-4′), 79.4 (C-3′), 84.1 (C-5′), 95.3 (C-1), 106.2 (C-2′), 131.1–131.6 (C$_6$H$_5$).

3′-O-Benzylsucrose (**4**): ^{1}H NMR (300 MHz, D_2O): δ = 3.40–3.58 (m, 3H, 4-H, 5-H, 2-H), 3.65 (s, 2H, 1′-H$_2$), 3.74 (dd, 1H, 3-H), 3.80–3.90 (m, 5H, 5′-H, 6′-H$_2$, 6-H$_2$), 4.20 (dd, 1H, 4′-H), 4.21 (d, 1H, 3′-H), 4.79 (s, 2H, CH_2 of Bn), 5.42 (d, 1H, 1-H), 7.39–7.49 (m, 5H, C$_6$H$_5$); $J_{1,2}$ = 3.8, $J_{2,3}$ = $J_{3,4}$ = 9.5, $J_{3',4'}$ = $J_{4',5'}$ = 8.4 Hz. – ^{13}C NMR (75.5 MHz, D_2O): δ = 62.9 (C-6), 65.0 (C-6′), 65.4 (C-1′), 72.0 (C-4), 73.9 (C-2), 75.1 (C-5), 75.6 (C-3), 76.0 (CH_2C$_6$H$_5$), 76.4 (C-4′), 84.2 (C-5′), 85.8 (C-3′), 94.8 (C-1), 106.7 (C-2′), 131.3–131.9 (C$_6$H$_5$).

Pyridinium Dichromate (PDC) on Alumina: Commercially available PDC (37.6 g, 0.1 mol) was dissolved in 100 ml of CH_2Cl_2 and neutral Al_2O_3 (63.4 g) was added gradually with vigorous stirring. The mixture was then taken to dryness on a rotary evaporator to provide an orange solid of sand-like consistency, 1 g corresponding to approximately 1 mmol of oxidant; it can be kept for weeks under vacuum in the dark without losing activity.

3,4,6,1′,3′,4′,6′-Hepta-O-benzoylsucrose (**5**): To a cooled solution (0°C) of the crude mixture of monobenzyl-sucroses as obtained above (4.20 g, 9.7 mmol) in pyridine (100 ml), 11.8 ml (102 mmol) of benzoyl chloride was added with stirring over 30 min, followed by standing at ambient temp. for about 12 h. It was then stirred into iced water, extracted with *tert*-butyl methyl ether (2 × 150 ml), the combined extracts were washed successively with 2 N HCl, water, and satd. $NaHCO_3$ and then dried (Na_2SO_4). Concentration of the extracts afforded a syrup which was purified by elution from a silica gel column (5 × 30 cm) with an eluant gradient from toluene to toluene/EtOAc (15:1); removal of the solvents from the eluates in vacuo gave 7.30 g (65%) of a mixture of perbenzoylated sucrose monobenzylethers, containing about 90% of the **2**-heptabenzoate; R_f = 0.40 in B. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (dd, 1H, 2-H), 5.52 (dd, 1H, 4-H), 5.84 (d, 1H, 1-H), 6.01 (dd, 1H, 3-H), 6.04 (dd, 1H, 4′-H), 6.14 (d, 1H, 3′-H), 7.05–8.24 (m, 35H, 7 C$_6$H$_5$); $J_{1,2}$ = 3.4, $J_{2,3}$ = 9.8, $J_{3,4}$ = $J_{4,5}$ = 9.8, $J_{3',4'}$ = $J_{4',5'}$ = 6.6 Hz.

A solution of 6.4 g (5.5 mmol) of the crude **2**-heptabenzoate in EtOAc (200 ml) was hydrogenated over 10% Pd/C (200 mg) at ambient temperature for 3 d. Filtration and removal of the solvent left a syrup, which was purified by elution from a silica gel column with toluene/EtOAc (15:1): 4.40 g (75%) of **5** as a colorless syrup; R_f = 0.26 in B, $[\alpha]_D^{20}$ = +21.5 (*c* = 1.2, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.97 (m, 1H, 2-H, 4.40 (dd, 1H, 6-H), 4.58–4.86 (m, 6H, 6-H_2, 1′-H_2, 5′-H, 6′-H_2), 5.63 (m, 2H, 3-H, 4-H), 5.83 (d, 1H, 1-H), 6.02 (dd, 1H, 4′-H), 6.08 (d, 1H, 3′-H), 7.22–8.16 (m, 35H, 7 C_6H_5); $J_{1,2}$ = 3.7, $J_{5,6}$ = 4.2, $J_{6,6}$ = 12.9, $J_{3',4'}$ = 5.6, $J_{4',5'}$ = 5.5, $J_{2,OH}$ = 8.0 Hz. – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 62.6 (C-6), 64.3 (C-6′), 65.1 (C-1′), 68.5 (C-4), 69.3 (C-5), 71.1 (C-2), 73.7 (C-3), 76.6 (C-4′), 77.9 (C-3′), 79.6 (C-5′), 93.2 (C-1), 104.5 (C-2), 128.3–133.7 (C_6H_5), 165.1–166.6 (CO). – $C_{61}H_{52}O_{18}$ (1071.1): calcd. C 68.41, H 4.71; found C 68.17, H 4.66.

3,4,6,1′,3′,4′,6′-Hepta-O-acetylsucrose (**6**): To a stirred and cooled (0°C) solution of the crude monobenzyl sucroses (4.35 g, 10 mmol, as obtained above) in pyridine (125 ml), a trace of 4-dimethylaminopyridine (5 mg) was added followed by the dropwise addition of acetic anhydride (11 ml, 11.6 mmol) and stirring at room temp. for about 12 h. Quenching by stirring into ice water, extraction with *tert*-butyl methyl ether (2 × 100 ml), successive washing of the combined extracts with 2 N HCl, satd. $NaHCO_3$, and water, drying (Na_2SO_4), and removal of the solvent gave a syrupy residue that was purified by elution from a silica gel column with toluene/EtOAc (2:1): 5.45 g (75%) of **2**-heptaacetate, containing less than 5% each of the peracetates of **3** and **4**; it was dissolved in EtOAc (100 ml), and hydrogenated over 10% Pd/C for 15 h at room temp. Filtration, evaporation of the solvent from the filtrate and crystallization from 2-propanol afforded **6** as colorless crystals: 3.85 g (80%, 42% for the three steps from sucrose); R_f = 0.24 in C, m.p. 114°C, $[\alpha]_D^{20}$ = +68.0 (*c* = 1.0, $CHCl_3$); lit.[32]: m.p. 110–114°C, $[\alpha]_D^{25}$ = +46.7 (*c* = 1.0, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): d = 2.04–2.21 (7 s, 3H each, 7 Ac-CH_3), 3.71 (dd, 1H, 2-H), 4.13–4.36 (m, 8H, 5-H), 6-H_2, 1′-H_2, 5′-H, 6′-H_2), 5.03 (dd, 1H, 4-H), 5.17 (dd, 1H, 3-H), 5.42–5.46 (m, 2H, 3′-H and 4′-H), 5.55 (d, 1H, 1-H); $J_{1,2}$ = 3.8, $J_{2,3}$ = $J_{3,4}$ = 9.7, $J_{4,5}$ = 9.6, $J_{3',4'}$ = $J_{4',5'}$ = 5.7 Hz; the data correlate well with those reported previously[32,33] for an enzymatic mono-deacylation product of octaacetyl sucrose. – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.7–21.0 (Ac-*C*H_3), 61.8 (C-6), 63.3 (C-6′), 63.5 (C-1′), 67.8 (C-4), 68.9 (C-5), 70.3 (C-2), 73.0 (C-3), 74.7 (C-4′), 76.3 (C-3′), 79.0 (C-5′), 92.4 (C-1), 103.8 (C-2′), 169.7–171.2 (Ac–*C*O). – MS (FD): *m/z* = 331 (tetra-*O*-acetyl-fructofuranosyl$^+$). – $C_{26}H_{36}O_{18}$ (636.6): calcd. C 49.06, H 5.70; found C 49.01, H 5.69.

Hepta-O-benzoyl-2-oxosucrose [(1,3,4,6-Tetra-O-benzoyl-β-D-fructofuranosyl)-3,4,6-tri-O-benzoyl-α-D-arabino-hexopyranosid-2-ulose] (**7**): To a vigorously stirred solution of 2.50 g (23 mmol) of **5** in CH_2Cl_2 (50 ml), freshly powdered molecular sieve (4 Å, 5 g) was added; PDC on alumina was then added in four portions over 30 min. After stirring at room temp. for 4 h, the solvent was removed by evaporation in vacuo and the residue was liberated from the chromium salts by flash-chromatography on silica gel (4 × 20 cm). Concentration of the appropriate eluate gave 1.92 g (77%) of **7** as a colorless foam; R_f = 0.44 in E, $[\alpha]_D^{20}$ = +6.0 (*c* = 0.9, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.46 (dd, 1H, 6-H_a), 4.66 (ddd, 1H, 5′-H), 4.71–4.84 (m, 5H, 6-H_b, 1′-H_2, 6′-H_2), 4.92 (ddd, 1H, 5-H), 5.79 (s, 1H, 1-H), 5.89 (dd, 1H, 4-H), 5.98 (dd, 1H, 4′-H), 6.08 (d, 1H, 3′-H), 6.10 (d, 1H, 3-H), 7.23–8.14 (m, 35H, 7 C_6H_5); $J_{3,4}$ = 10.3, $J_{4,5}$ = 10.1, $J_{5,6a}$ = 3.8, $J_{6,6}$ = 12.6, $J_{3',4'}$ = $J_{4',5'}$ = 5.2 Hz. – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 62.0 (C-6), 64.2 (C-6′), 64.5 (C-1′), 69.7 (C-4), 69.9 (C-5), 75.1 (C-3), 76.9 (C-4′), 78.0 (C-3′), 80.1 (C-5′), 93.3 (C-1), 105.2 (C-2′), 128.2–133.6 (C_6H_5), 164.4–165.9 (CO), 191.4 (C-2). – $C_{61}H_{48}O_{18}$ (1069.0): calcd. C 68.53, H 4.53; found C 68.35, H 4.57.

(1,3,4,6-Tetra-O-benzoyl-β-D-fructofuranosyl)-3,4,6-tri-O-benzoyl-2-(hydroxyimino)-α-D-arabino-hexopyranoside (**8**, Oxime of 2-Oxosucrose Heptabenzoate): To a solution of **7** (1.5 g, 1.4 mmol) in pyridine (20 ml), $NH_2OH \cdot HCl$ (150 mg, 2.1 mmol), was added and the mixture was kept at ambient temperature for about 15 h. It is then stirred into iced water, extracted with *t*-butyl methyl ether (2 × 100 ml), the combined extracts were washed successively with 2 N HCl, a satd. $NaHCO_3$ solution, and water and then dried (Na_2SO_4). Removal of the solvent gave a crude product which was purified by elution from a silica gel column (3.5 × 30 cm) with toluene/EtOAc (10:1). Concentration of the eluates afforded 1.2 g (81%) of oxime **8** as a syrup; R_f = 0.47 in E, $[\alpha]_D^{20}$ = +3.5 (*c* = 1.0, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.47 (dd, 1H, 6-H_a), 4.60–4.83 (m, 6H, 5-H, 6-H_b, 1′-H_2, 6′-H_2), 5.77 (dd, 1H, 4-H), 6.00 (dd, 1H, 4′-H), 6.08 (d, 1H, 3′-H), 6.17 (d, 1H, 3-H), 6.82 (s, 1H, 1-H), 7.18–8.19 (m, 35H, 7 C_6H_5); $J_{3,4}$ = $J_{4,5}$ = 10.0, $J_{5,6}$ = 3.4, $J_{6,6}$ = 12.2, $J_{3',4'}$ = 5.5, $J_{4',5'}$ = 5.2 Hz. – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 62.5 (C-6), 64.4 and 64.6 (C-1′ and C-6′), 69.7 (C-3, C-4, C-5), 77.4 (C-4′), 77.9 (C-3′), 79.9 (C-5′), 84.5 (C-1), 104.8 (C-2′), 128.3–133.6 (C_6H_5), 148.2 (C-2), 164.8–166.1 (CO). – MS (FD, 20 mA): *m/z* = 578 (tetra-*O*-benzoylfructofuranosyl$^+$).

(1,3,4,6-Tetra-O-benzoyl-β-D-fructofuranosyl)-3,4,6-tri-O-benzoyl-2-benzoyloxyimino-α-D-arabino-hexopyranoside (**9**, *O*-Benzoyloxime of 2-Oxosucrose Heptabenzoate): Benzoyl chloride (1.5 ml) was added to a solution of oxime **8** and the mixture was stirred at ambient temp. for 15 h. Removal of the solvent in vacuo and purification of the residue by elution from a silica gel column with toluene/EtOAc (20:1) gave 610 mg (93%) of **9**; R_f = 0.50 in E, $[\alpha]_D^{20}$ = +29.1 (*c* = 1.1, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.44 (dd, 1H, 6-H_a), 4.70 (d, 1H, 1′-H_a), 4.76–4.86 (m, 5H, 5-H, 6-H_b, 5′-H, 6′-H_2), 4.91 (d, 1H, 1′-H_b), 5.97 (dd, 1H, 4-H), 6.10–6.16 (m, 2H, 3′-H, 4′-H), 6.38 (d, 1H, 3-H), 7.11 (s, 1H, 1-H), 7.19–8.25 (m, 40H, 8 C_6H_5); $J_{3,4}$ = $J_{4,5}$ = 10.0, $J_{5,6a}$ = 3.5, $J_{6,6}$ = 12.4, $J_{1,1}$ = 12.0 Hz. – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 62.2 (C-6), 63.9 and 64.6 (C-1′ and C-6′), 69.7 (C-5), 69.8 (C-4), 69.9 (C-3), 75.8 (C-4′), 77.9 (C-3′), 79.7 (C-5′), 85.1 (C-1), 104.9 (C-2′), 127.8–133.8 (C_6H_5), 155.7 (C-2), 162.3–166.1 (CO). – MS (FD, 20 mA): *m/z* = 1187 (M^+). – $C_{68}H_{53}NO_{19}$ (1188.2): calcd. C 68.74, H 4.50, N 1.18; found C 67.80, H 4.42, N 1.17.

(2R,6S)-4-Benzoyloxy-6-benzoyloxymethyl-2-(1,3,4,6-tetra-O-benzoyl-β-D-fructofuranosyloxy)-2H-pyran-3(6H)-one (**10**): Sodium hydrogen carbonate (100 mg) was suspended in a solution of 500 mg (0.47 mmol) 2-keto-sucrose **7** in acetonitrile (10 ml) and the mixture was stirred for 1 h at ambient temp. Filtration, removal of the solvent, and purification by eluation from a silica gel column (2 × 25 cm) with toluene/EtOAc (20:1) afforded 394 mg (89%) dihydropyranone **10** as a colorless foam; R_f = 0.49 in F, $[\alpha]_D^{20}$ = –20.7 (*c* = 1.1, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.47 (dd, 1H, 7-H_a), 4.56 (dd, 1H, 7-H_b), 4.64 and 4.80 (2 d, 1H each, 1′-H_2), 4.69–4.85 (m, 3H, 5′-H, 6′-H_2), 5.38 (ddd, 1H, 6-H), 5.86 (s, 1H, 2-H), 6.00 (dd, 1H, 4′-H), 6.10 (d, 1H, 3′-H), 6.71 (s, 1H, 5-H), 7.23–8.15 (m, 30H, 6 C_6H_5); $J_{5,6}$ = 1.8, $J_{6,7}$ = 4.8 and 5.0, $J_{7'a,7'b}$ = 11.7, $J_{1'a,1'b}$ = 12.3, $J_{3',4'}$ = 6.3, $J_{4',5'}$ = 5.8 Hz. – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 64.2 (C-7), 64.4 (C-6′), 64.8 (C-1′), 68.4 (C-6), 76.4 (C-4′), 77.4 (C-3′), 79.4 (C-5′), 92.1 (C-2), 104.4 (C-2′), 128.1–133.6 (C_6H_5), 141.7 (C-4), 163.2–165.8 (CO), 181.4 (C-3). – MS (FD, 20 mA): *m/z* = 946 (M^+). – $C_{54}H_{42}O_{16}$ (946.9): calcd. C 68.49, H 4.47; found C 68.42, H 4.33.

3,4,6,1′,3′,4′,6′-Hepta-O-acetyl-2-O-[(1-imidazolyl)thiocarbonyl]sucrose: A solution of 2.1 g (3.3 mmol) heptaacetyl su-

crose **6** and 2.1 g (11.8 mmol) *N,N*-thiocarbonyldiimidazole in dry THF (30 ml) was refluxed for 14 h. Removal of the solvent and purification by elution from a silica gel column (3 × 30 cm) with toluene/EtOAc (2:5) afforded after removal of the solvents 2.1 g (87%) of the thiourethane as a colorless syrup; R_f = 0.34 in E, $[\alpha]_D^{20}$ = +59.0 (*c* = 1.0, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94–2.35 (7 s, 3H each, 7 Ac-CH_3), 4.10–4.29 (m, 7H, 6-H_2, 1′-H_2, 5′-H, 6′-H_2), 4.30–4.39 (m, 1H, 5-H), 5.22 (dd, 1H, 4-H), 5.34 (dd, 1H, 4′-H), 5.38 (d, 1H, 3′-H), 5.54 (dd, 1H, 2-H), 5.71 (dd, 1H, 3-H), 6.04 (d, 1H, 1-H), imidazole-H at 7.04 (m, 1H), 7.57 (t, 1H), and 8.32 (s, 1H); $J_{1,2}$ = 3.6, $J_{2,3}$ = 10.2, $J_{3,4}$ = $J_{4,5}$ = 9.8, $J_{3',4'}$ = $J_{4',5'}$ = 5.6 Hz. – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.3–21.4 (CH_3 of Ac), 61.4 (C-6), 63.1 (C-1′ and C-6′), 68.1 (C-4), 68.8 (C-5), 69.4 (C-3), 74.7 (C-4′), 75.8 (C-3′), 77.7 (C-2), 78.9 (C-5′), 88.8 (C-1), 104.2 (C-2′), 117.9, 131.5, and 137.4 (imidazolyl-*C*), 169.3–170.6 (CO of Ac), 183.1 (*C*S). – MS (FD): *m/z* = 746 (M^+). – $C_{30}H_{38}N_2O_{18}S$ (746.7): calcd. C 48.26, H 5.13, N 3.75; found C 48.17, H 5.06, N 3.68.

Hepta-O-acetyl-2-deoxysucrose (**11**): A solution of 0.74 ml (2.76 mmol) tributyltin hydride in 20 ml of dry toluene with freshly desiccated molecular sieve (4 Å) were refluxed under an atmosphere of nitrogen and 700 mg (0.92 mmol) thiourethane, dissolved in 15 ml absolute toluene, were added dropwise for 90 min. After stirring for another 90 min. the reaction mixture was allowed to cool down to room temp., and after removal of the solvent, the resulting residue was dissolved in dry acetonitrile (50 ml) and thoroughly washed with pentane (4 × 50 ml). The solvent was removed in vacuo and the resulting syrup was further purified by elution from a silica gel column (3 × 30 cm) with toluene/EtOAc (2:1). Concentration of the appropriate eluates gave 470 mg (81%) of **11** as a colorless syrup; R_f = 0.40 in E, $[\alpha]_D^{20}$ = +34.3 (*c* = 1.0, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.87 (ddd, 1H, 2-H_{ax}), 2.01–2.17 (m, 22H, 7 CH_3 of Ac and 2-H_{eq}), 4.12–4.36 (m, 8H, 5-H, 6-H_2, 1′-H_2, 5′-H, 6′-H_2), 5.03 (dd, 1H, 4-H), 5.28 (ddd, 1H, 3-H), 5.43 (m, 2H, 3′-H, 4′-H), 5.59 (m, 1H, 1-H); $J_{1,2a}$ = 3.5, $J_{2,2}$ = 12.7, $J_{2a,3}$ = 12.0, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz. – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.6–20.9 (Ac-*C*H_3), 35.7 (C-2), 62.1 (C-6), 63.4 (C-6′), 63.5 (C-1′), 68.8 (C-4), 68.9 (C-3), 69.3 (C-5), 74.7 (C-4′), 75.9 (C-3′), 78.5 (C-5′), 91.1 (C-1), 103.3 (C-2′), 169.7–170.8 (CO of Ac). – MS (FD): *m/z* = 620 (M^+).

2-Deoxysucrose (**12**): To a solution of 450 mg (0.725 mmol) of **11** in 20 ml of MeOH 10 mg of sodium methoxide was added. After stirring for 4 h at room temp. the reaction mixture was neutralized by addition of a strongly acidic ion-exchange resin (Amberlite IR-120, H^+ form), which had been thoroughly prewashed with water and MeOH. After filtration and removal of the solvent, the resulting syrup was purified by elution from a silica gel column with $CHCl_3$/MeOH (3:2) to yield 210 mg (90%) of **12** as a colorless, hygroscopic foam; R_f = 0.20 in A, $[\alpha]_D^{20}$ = +47.2 (*c* = 1.0, H_2O); lit.[17] $[\alpha]_D^{20}$ = +45.9 (*c* = 0.7, H_2O) for an enzymatically prepared sample. – ^{1}H NMR (300 MHz) (a) in D_2O: δ = 1.73 (ddd, 1H, 2-H_a), 2.06 (dd, 1H, 2-H_e), 3.40 (dd, 1H, 4-H), 3.67 (s, 2H, 1′-H_2), 3.78–3.93 (m, 6H, 5-H, 6-H_2, 5′-H, 6′-H_2), 3.99 (ddd, 1H, 3-H), 4.06 (dd, 1H, 4′-H), 4.17 (d, 1H, 3′-H), 5.54 (d, 1H, 1-H); $J_{1,2}$ = 1.8 and 3.5, $J_{2,2}$ = 13.0, $J_{2,3}$ = 3.5 and 12.0, $J_{3,4}$ = $J_{4,5}$ = 9.0, $J_{3',4'}$ = 8.7, $J_{4',5'}$ = 8.5 Hz; (b) in $[D_6]$DMSO: δ = 1.44 (ddd, 1H, 2-H_a), 1.76 (dd, 1H, 2-H_e), 3.03 (dd, 1H, 4-H), 3.33 (s, 2H, 1′-H_2), 3.44–3.65 (m, 7H, 5-H, 6-H_2, 5′-H, 6′-H_2, 3-H), 3.84 (dd, 1H, 4′-H), 3.95 (d, 1H, 3′-H), 5.44 (d, 1H, 1-H); $J_{1,2}$ = 1.8 and 3.5, $J_{2,2}$ = 12.8, $J_{2,3}$ = 3.6 and 12.4, $J_{3,4}$ = $J_{4,5}$ = 9.0, $J_{3',4'}$ = 8.3, $J_{4',5'}$ = 8.0 Hz. – ^{13}C NMR (75.5 MHz) (a) in D_2O: δ = 40.7 (C-2), 63.1 (C-6), 63.6 (C-1′), 65.1 (C-6′), 70.8 (C-3), 73.5 (C-4), 75.8 (C-5), 76.7 (C-4′), 78.8 (C-3′), 84.0 (C-5′), 94.1 (C-1), 106.7 (C-2′); (b) in $[D_6]$DMSO: δ = 45.5 (C-2), 60.7 (C-6), 61.5 (C-6′), 61.7 (C-1′), 67.5 (C-3), 71.6 (C-4), 73.3 (C-5 and C-4′), 75.7 (C-3′), 81.9 (C-5′), 89.9 (C-1), 104.3 (C-2′). – MS (FD): *m/z* = 349 (MNa^+).

N-Acetyl-hepta-O-benzoylsucrosamine (**13**, Hepta-*O*-benzoyl-2-acetamido-2-deoxysucrose) *and (1,3,4,6-Tetra-O-benzoyl-β-*D*-fructopyranosyl)-2-acetamido-3,4,6-tri-O-benzoyl-2-deoxy-α-*D*-mannopyranoside* (**15**): To a stirred and cooled (–10°C) solution of the benzoyl oxime **9** (600 mg, 0.5 mmol) in dry THF (20 ml) a 1.0 M solution of diborane in THF (10 ml, 10 mmol) under an atmosphere of nitrogen was added. After 1 h the mixture was allowed to warm to room temp. and stirred for another 4 h. The remaining diborane was then destroyed by the addition of MeOH (4 ml), and acetic anhydride (4 ml) was added for *N*-acetylation. After standing for about 12 h the solvents were removed to give 470 mg (85%) of an approximate 2:1 mixture of **13** and **15**, which was separated by elution from a silica gel column (2.5 × 20 cm) with toluene/EtOAc (2:1). Removal of the eluant of the fractions with R_f = 0.55 (in G) yielded 265 mg (48%) of **13** as a colorless solid; $[\alpha]_D^{20}$ = +16.5 (*c* = 1.1, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.57 (s, 3H, Ac-CH_3), 4.30 and 4.51 (2 dd, 1H each, 6-H_2), 4.60–4.82 (m, 5H, 5-H, 5′-H, 6′-H_2, 2-H), 4.75 and 4.87 (2 d, 1H each, 1-H_2), 5.59 (dd, 1H, 4-H), 5.71 (dd, 1H, 3-H), 5.80 (d, 1H, 1-H), 5.95 (dd, 1H, 4′-H), 6.02 (d, 1H, 3′-H), 6.08 (d, 1H, NH), 7.17–8.23 (m, 35H, 7 C_6H_5): $J_{1,2}$ = 3.5, $J_{2,3}$ = 9.8, $J_{3,4}$ = 10.3, $J_{4,5}$ = 10.5, $J_{3',4'}$ = 4.7, $J_{4',5'}$ = 4.9, $J_{2,NH}$ = 9.2 Hz. – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 22.6 (CH_3 of Ac), 52.4 (C-2), 62.3 (C-6), 64.1 (C-1′), 64.4 (C-6′), 68.8 (C-4), 69.5 (C-3), 71.3 (C-5), 77.1 (C-4′), 78.1 (C-3′), 79.9 (C-5′), 92.7 (C-1), 104.9 (C-2′), 128.2–133.7 (C_6H_5), 164.9–166.5 (CO), 170.2 (CO of Ac). – MS (FD, 20 mA): *m/z* = 1111 (M^+). – $C_{63}H_{53}NO_{18}$ (1112.1): calcd. C 68.04, H 4.80, N 1.26; found C 67.95, H 4.72, N 1.20.

Concentration of the fractions with R_f = 0.32 in G gave 149 mg (29%) **15** as an amorphous solid; $[\alpha]_D^{20}$ = –11.0 (*c* = 1.0, $CHCl_3$). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.81 (s, 3H, CH_3 of Ac), 4.38–4.47 (2 dd, 1H each, 6-H_2), 4.69 and 4.78 (2 d, 1H each, 1-H_2), 4.57–4.88 (m, 5H, 2-H, 5-H, 5′-H, 6′-H_2), 5.64 (dd, 1H, 4-H), 5.68 (d, 1H, 1-H), 5.78 (dd, 1H, 3-H), 5.85 (d, 1H, NH), 5.94 (dd, 1H, 4′-H), 5.99 (d, 1H, 3′-H), 7.23–8.11 (m, 35H, 7 C_6H_5); $J_{1,2}$ = 1.8, $J_{2,3}$ = 4.2, $J_{3,4}$ = $J_{4,5}$ = 10.3, $J_{3',4'}$ = 6.0, $J_{4',5'}$ = 5.8, $J_{2,NH}$ = 7.8 Hz. – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.2 (CH_3 of Ac), 52.0 (C-2), 63.2 (C-6), 64.7 (C-1′ and C-6′), 66.8 (C-4), 69.6 (C-3), 69.9 (C-5), 76.8 (C-3′), 78.0 (C-4′), 79.5 (C-5′), 93.1 (C-1), 104.6 (C-2′), 128.5–133.7 (C_6H_5), 165.2–166.1 (CO), 170.1 (CO of Ac). – MS (FD, 20 mA): *m/z* = 1111 (M^+). – $C_{63}H_{53}NO_{18}$ (1112.1): calcd. C 68.04, H 4.80, N 1.26; found C 67.67, H 4.70, N 1.21.

2-Acetamido-2-deoxysucrose (**14**, *N*-Acetylsucrosamine): To a methanolic solution of heptabenzoate **13** (110 mg in 10 ml) sodium methoxide (15 mg) was added, and the mixture was stirred at ambient temperature for 5 h. Neutralization (Amberlite IR-120, H^+-form), filtration, concentration of the filtrate in vacuo, elution of the residual syrup from a silica gel column (1 × 20 cm) with $CHCl_3$/MeOH (2:1) afforded 32 mg (87%) of **14** as a colorless syrup; R_f = 0.35 in A, $[\alpha]_D^{20}$ = +83.6 (*c* = 1.4, H_2O); ref.[16] m.p. 178–180°C, $[\alpha]_D^{20}$ = +71 (*c* = 0.5, H_2O). – ^{1}H NMR (300 MHz, D_2O): δ = 2.06 (s, 3H, CH_3 of Ac), 3.50 (d, 1H, 1′-H_a), 3.54 (dd, 1H, 4-H), 3.60 (d, 1H, 1′-H_b), 3.76–3.91 (m, 8H, 6′-H_2, 6-H_2, 5-H, 5′-H, 2-H, 3-H), 4.03 (dd, 1H, 4′-H), 4.23 (d, 1H, 3′-H), 5.39 (d, 1H, 1-H); $J_{1,2}$ = 3.5, $J_{3,4}$ = $J_{4,5}$ = 9.1, $J_{1',1'}$ = 12.1, $J_{3',4'}$ = $J_{4',5'}$ = 8.5 Hz. – ^{13}C NMR (75.5 MHz, D_2O): δ = 24.7 (CH_3 of Ac), 56.6 (C-2), 62.9 (C-6′), 63.6 (C-1′), 65.1 (C-6), 72.4 (C-4), 73.1 (C-3), 75.3 (C-5), 76.5 (C-4′), 78.4 (C-3′), 84.2 (C-5′), 93.6 (C-1),

106.6 (C-2′), 177.3 (CO of Ac). – $C_{14}H_{25}NO_{11}$ (383.35): calcd. C 43.86, H 6.57, N 3.65; found C 43.91, H 6.74, N 3.60.

β-D-Fructofuranosyl-2-acetamido-2-deoxy-α-D-mannopyranoside (**16**): De-*O*-benzoylation of **15** (150 mg) was effected by exposure to sodium methoxide in methanol as described for **13** → **14**, to give, upon purification by elution from a silica gel column (1 × 20 cm) with $CHCl_3$/MeOH (2:1), 43 mg (84%) of **16** as a uniform syrup; R_f = 0.30 in A, $[\alpha]_D^{20}$ = −4.0 (*c* = 0.8, H_2O). – ^1H NMR (300 MHz, D_2O): δ = 2.06 (s, 3H, CH_3 of Ac), 3.62–3.74 (m, 3H, 1′-H_2, 4-H), 3.78–3.92 (m, 6H, 6′-H_2, 6-H_2, 5-H, 5′-H), 4.05 (dd, 1H, 4′-H), 4.11 (dd, 1H, 3-H), 4.20 (d, 1H, 3′-H), 4.23 (dd, 1H, 2-H), 5.31 (d, 1H, 1-H); $J_{1,2}$ = 1.6, $J_{2,3}$ = 4.7, $J_{3,4}$ = 9.8, $J_{3',4'}$ = $J_{4',5'}$ = 8.6 Hz. – ^{13}C NMR (75.5 MHz, D_2O): δ = 24.7 (CH_3 of Ac), 56.7 (C-2), 62.9 (C-6′), 63.5 (C-1′), 65.2 (C-6), 69.2 (C-4), 71.5 (C-3), 75.8 (C-5), 76.7 (C-4′), 78.7 (C-3′), 84.2 (C-5′), 95.4 (C-1′), 107.1 (C-2′), 177.7 (CO of Ac). – $C_{14}H_{25}NO_{11}$ (383.35): calcd. C 43.86, H 6.57, N 3.65; found C 43.74, H 6.08, N 3.61.

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