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Crystal and molecular structures of β-cellobiosylnitromethane and of β-maltosylnitromethane heptaacetate

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ABSTRACT

The structures of the title compounds have been determined by X-ray crystallography, using direct methods, and have been refined to conventional final residual factors of $R = 0.063$ and $R = 0.046$, respectively.

INTRODUCTION

The addition of nitromethane to reducing sugars, called the Fischer–Sowden reaction[1], is an important reaction for chain elongation in carbohydrate chemistry. The resulting mixture of two epimeric nitroalditols can be cyclodehydrated easily to a mixture of 2,5- and 2,6-anhydro-1-deoxy-1-nitroalditols by heating in water. From these mixtures, the thermodynamically most stable isomer, usually the "β-glycopyranosylnitromethane", can be isolated in high yields. Thus, β-cellobiosylnitromethane (**1**) and β-maltosylnitromethane were obtained in a simple procedure from the respective reducing disaccharides[2]. Whereas in our hands, **1** yielded crystals suitable for conventional X-ray analysis, the corresponding crystalline maltosyl derivative, because of the small size of individual crystals, had to be acetylated to the heptaacetate **2** to enable a similar investigation.

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TABLE I

Crystallographic data for **1** and **2** [a]

Data	**1**	**2**
Formula	$C_{13}H_{23}NO_{12}$	$C_{27}H_{37}NO_{19}$
Mol wt	385.32	679.58
Mp (°C)	231–238 (dec)	190.5–191.5
Crystal dimensions (mm)	0.4×0.4×0.3	0.5×0.3×0.3
Space group	$P2_12_12_1$	$P2_1$
Cell parameters (pm, degrees)		
a	724.6(1)	562.4(1)
b	924.3(1)	1387.9(2)
c	2454.4(3)	2174.2(3)
β		92.45(2)
Volume V (pm^3)	$1643.8(4)\times10^6$	$1695.6(5)\times10^6$
Z	4	2
$F(000)$	816	716
Calculated density D_x ($g\ cm^{-3}$)	1.557	1.331
λ(Cu-$K\alpha_1$)(pm)	154.178	154.178
μ (cm^{-1})	12.2	9.9
2θ range (degrees)	4.5–153	4.5–153
Reflections measured	4147	6955
Symmetry independent reflections	3437	6193
Reflections with $I > 2\sigma(I)$	3279	5182
Number of refined parameters	266	469
Final conventional residual factor R_{obsd}	0.063	0.046
Goodness of fit S_{obsd}	1.04	1.05
Diffractometer	Enraf-Nonius CAD 4	Enraf-Nonius CAD 4

[a] Standard deviations in parentheses.

RESULTS AND DISCUSSION

Both **1** and **2** crystallized from ethanol. Relevant crystallographic data are given in Table I.

The structures were solved by direct methods with the program SHELXS-90[3] and refined with SHELXL-92[4]. The refinement was done on F^2 for all reflections. The validated threshold $I > 2\sigma(I)$ was used for calculating R_{obsd} only.

All atoms, with hydrogens introduced at theoretical positions using the AFIX option[4,*], were refined. The final fractional coordinates of C, N, and O with equivalent isotropic thermal parameters are listed in Tables II and III**. Molecules of **1** and **2** are presented in Figs. 1 and 2 (SCHAKAL-88 drawings[5]), respectively,

* If hydrogens are introduced by using the AFIX option and refined as riding on the heavy atom at a fixed distance, e.s.d.'s for bond lengths and angles involving hydrogens are calculated probably an order of magnitude too low.

** Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

TABLE II

Fractional positional parameters of C, N, and O atoms ($\times 10^4$) and the temperature factors U_{eq} [a] ($\times 10^3$) for **1** [b]

Atom	β-D-Glucosyl moiety				Atom	2,6-Anhydronitroheptitol moiety			
	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
					N-1′	−3403(4)	2715(3)	−299(1)	44(2)
					C-1′	−4287(4)	4079(3)	−485(1)	40(1)
					O-11′	−2602(7)	1969(4)	−618(1)	99(4)
					O-12′	−3659(8)	2362(5)	162(2)	124(5)
O-1	81(3)	8362(2)	−1428(1)	31(1)					
O-2	3108(4)	10073(3)	−1086(1)	62(1)	O-3′	−5416(4)	5421(3)	−1496(1)	55(2)
O-3	3654(4)	12605(3)	−1710(1)	56(1)	O-4′	−4006(3)	8304(3)	−1647(1)	45(1)
O-4	206(4)	14055(2)	−2004(1)	51(1)					
O-5	−1054(3)	10240(2)	−1916(1)	32(1)	O-2′	−1682(3)	5604(2)	−510(1)	34(1)
O-6	−4193(4)	11155(3)	−2423(1)	55(1)	O-7′	2140(4)	5897(3)	−161(1)	57(1)
C-1	39(4)	9860(3)	−1450(1)	29(1)	C-2′	−3037(4)	4959(3)	−850(1)	32(1)
C-2	1992(5)	10447(3)	−1532(1)	38(1)	C-3′	−4153(4)	6130(3)	−1142(1)	33(1)
C-3	1846(4)	12091(3)	−1586(1)	36(1)	C-4′	−2892(4)	7140(3)	−1451(1)	32(1)
C-4	484(5)	12533(3)	−2023(1)	35(1)	C-5′	−1309(4)	7675(3)	−1095(1)	28(1)
C-5	−1370(4)	11775(3)	−1955(1)	31(1)	C-6′	−342(4)	6431(3)	−801(1)	30(1)
C-6	−2614(5)	12022(3)	−2442(1)	41(1)	C-7′	1013(5)	6989(4)	−384(1)	41(1)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$. [b] Standard deviations in parentheses.

showing the atom numbering schemes as well. Compound **1** is composed of a β-D-glucosyl group linked to 2,6-anhydro-1-deoxy-1-nitro-D-*glycero*-D-*gulo*-heptitol as the "aglycon" via position 5. The numbering scheme was chosen with respect to this nomenclature. In Table II, entries for related atoms of these two moieties are given in the same line. Besides being acetylated at the hydroxyl groups, compound **2** differs only in the configuration of the glycosidic linkage (α configuration). The presentation of data for compound **2** in Table III follows that of Table II.

The individual molecules of **1** are held together in the crystal by a complex pattern of strong hydrogen bonds, which is given in Table IV. Interestingly, the hydroxyl groups in positions 2 and 7′ do not participate either as hydrogen bond donors or as acceptors. A very strong intramolecular bond is observed between O-4′/H-4O′ and O-5. A similar situation has been reported for β-cellobiose[6]. Both pyranoid rings of **1** are found in $^4C_1$(D) chair conformations with all non-hydrogen substituents situated in equatorial positions. The puckering parameters according to the definitions of Cremer and Pople[7] are $Q = 58.6(3)$ pm, $\theta = 7.8(3)°$, and $\Phi = 44(2)°$ for the glycon, and $Q = 55.3(3)$ pm, $\theta = 5.7(3)°$, and $\Phi = 6(3)°$ for the "aglycon". Both primary hydroxyl groups are found in g^+, *t* orientations as was observed also for β-cellobiose[6]. The orientation of the nitromethyl group is as expected[8]. N-1′ is *gauche* to O-2′ and *trans* to C-3′. Of the oxygens, one is found more or less 1,2- and the other 1,3-parallel to a hydrogen atom. In accordance with the predictions of the exo-anomeric effect[9], which in this case is assisted by the aforementioned intramolecular hydrogen bond, C-5′ is found almost *trans* to C-2

TABLE III

Fractional positional parameters ($\times 10^4$) of C, N, and O atoms and the temperature factors U_{eq} [a] ($\times 10^3$) for **2** [b]

Atom	α-D-Glucosyl moiety				Atom	2,6-Anhydronitrohepitol moiety			
	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
					N-1′	7061(4)	−5034(2)	4758(1)	66(1)
					C-1′	5077(5)	−5530(2)	4418(1)	67(2)
					O-11′	8987(4)	−5022(3)	4534(1)	98(1)
					O-12′	6696(6)	−4661(3)	5242(1)	113(2)
O-1	1593(3)	−3698(1)	2295(1)	49(1)					
O-2	1404(3)	−4386(1)	1120(1)	56(1)	O-3′	3517(4)	−6648(1)	3352(1)	65(1)
O-3	1231(3)	−2644(2)	472(1)	56(1)	O-4′	−182(3)	−5653(1)	2590(1)	50(1)
O-4	1358(3)	−1020(2)	1304(1)	68(1)					
O-5	−1980(3)	−2843(1)	2129(1)	56(1)	O-2′	4176(3)	−4168(1)	3822(1)	54(1)
O-6	−2840(5)	−1060(2)	2832(1)	88(2)	O-7′	1318(3)	−2594(2)	3796(1)	71(1)
O-21	−1556(4)	−5256(3)	735(3)	150(1)	O-31′	102(7)	−7290(3)	3638(2)	121(2)
O-31	5198(3)	−2647(3)	521(1)	95(1)	O-41′	1718(4)	−6706(2)	2003(1)	81(1)
O-41	−1453(4)	−77(2)	861(2)	97(1)					
O-61	−473(25)	70(9)	2811(3)	378(2)	O-71′	3628(5)	−2080(3)	4586(1)	113(2)
C-1	−636(4)	−3650(2)	1967(1)	49(1)	C-2′	4735(4)	−5153(2)	3771(1)	52(1)
C-2	−147(4)	−3617(2)	1287(1)	47(1)	C-3′	2680(4)	−5693(2)	3441(1)	51(1)
C-3	1114(4)	−2691(2)	1132(1)	50(1)	C-4′	2041(4)	−5234(2)	2824(1)	47(1)
C-4	−244(4)	−1825(2)	1341(1)	52(1)	C-5′	1649(4)	−4149(2)	2885(1)	46(1)
C-5	−908(5)	−1930(2)	2011(1)	57(1)	C-6′	3752(4)	−3690(2)	3250(1)	50(1)
C-6	−2712(6)	−1173(3)	2177(2)	76(2)	C-7′	3341(5)	−2651(2)	3408(1)	63(2)
C-21	519(5)	−5127(2)	810(2)	67(1)	C-31′	2103(8)	−7394(3)	3481(2)	84(3)
C-22	2393(6)	−5799(3)	610(2)	79(2)	C-32′	3338(16)	−8329(4)	3391(4)	142(7)
C-31	3377(4)	−2657(2)	222(1)	56(1)	C-41′	−85(4)	−6423(2)	2213(1)	56(1)
C-32	3111(5)	−2672(3)	−455(1)	69(2)	C-42′	−2493(6)	−6849(3)	2091(2)	85(2)
C-41	555(5)	−193(3)	1039(2)	84(2)					
C-42	2500(9)	527(4)	1005(5)	157(3)					
C-61	−1863(14)	−353(5)	3089(3)	142(6)	C-71′	1741(6)	−2365(3)	4383(2)	76(2)
C-62	−2053(14)	−288(5)	3770(3)	133(6)	C-72′	−384(8)	−2499(4)	4762(2)	107(3)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$. [b] Standard deviations in parentheses.

and almost *gauche* to O-5. The torsion angles are 149.3(2)° and −93.1(2)°, respectively. For β-cellobiose[6], the values 166.5° and −76.3° have been reported[10].

The geometry of the β-maltose-derived heptaacetate **2** is given in Fig. 2. Again, not surprisingly, the two pyranoid rings are both found in $^4C_1$ chair conformations with all the non-hydrogen substituents situated in equatorial positions. The puckering parameters according to Crèmer and Pople[7] are $Q = 53.4(3)$ pm, $\theta = 4.9(3)°$, and $\Phi = 92(3)°$ for the glycon, and $Q = 54.7(3)$ pm, $\theta = 2.5(2)°$, and $\Phi = 11(6)°$ for the "aglycon". The two primary acetoxyl groups adopt different positions. As observed for β-maltose monohydrate[11], the orientation in the α-D-glucosyl moiety of **2** is g^+, t, whereas in the part with the β-D configuration it is g^-, g^+. The situation reported[12] for β-maltose octaacetate is more complicated. Whereas the conformation in the "reducing part" is again g^-, g^+, only half of the molecules exhibit a g^+, t conformation around C-6. The other C-6 acetates were claimed to

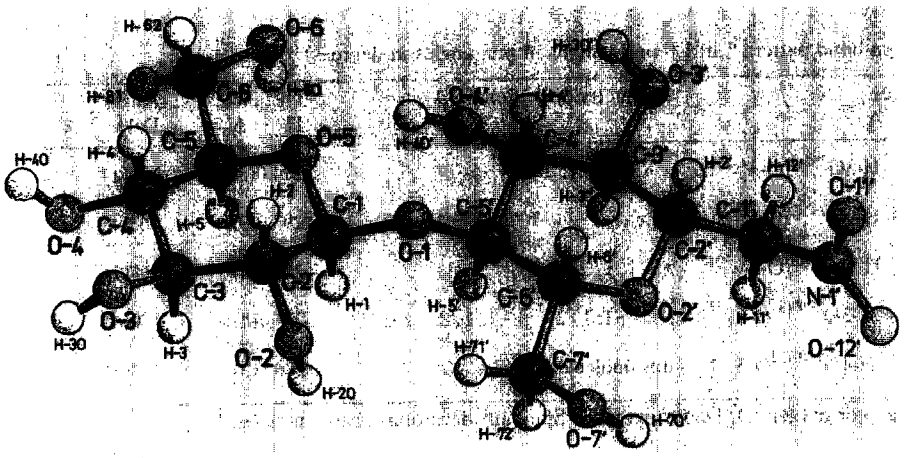

Fig. 1. SCHAKAL-88[5] plot of a molecule of **1**, giving the atom numbering scheme.

occupy t, g^- positions because of severe disorder. Disorder in this position was also observed in other acetylated saccharides[12]. Compound **2** is no exception, as can be seen from Table III. The temperature factors of atoms C-61, C-62, and O-61 are very high, but not that of O-6. Contrary to the situation in β-maltose octaacetate, this is not indicative of a totally different orientation of the acetoxyl group in the aforementioned position of the molecules. The situation observed for

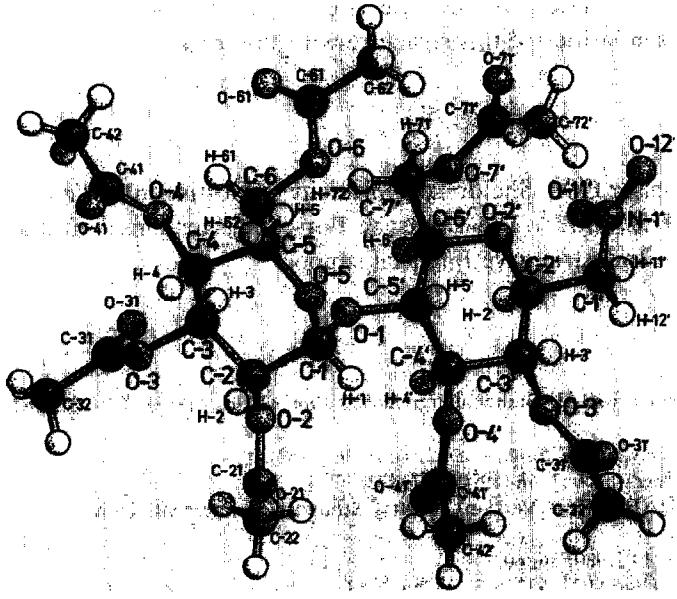

Fig. 2. SCHAKAL-88[5] plot of a molecule of **2**, giving the atom numbering scheme (except that for the hydrogens of the acetyl groups).

TABLE IV

Hydrogen-bond pattern [a] in **1** (bond lengths in pm, angles in degrees) [b]

Distances D-H···A	Symmetry operation on A	Distance D···A	Angle D-H···A
O-3 $\overset{85(2)}{\longrightarrow}$ H-3O$^{191(1)}$O-3′	$x+1, y+1, z$	274.0(4)	164(1)
O-4 $\overset{85(3)}{\longrightarrow}$ H-4O$^{211(3)}$O-5	$-x, 1/2+y, 1/2-z-1$	293.3(3)	163(4)
O-6 $\overset{85(7)}{\longrightarrow}$ H-6O$^{187(8)}$O-3	$x-1, y, z$	270.0(4)	167(7)
O-3′ $\overset{85(2)}{\longrightarrow}$ H-3O′$^{199(3)}$O-6	$-x-1, 1/2+y-1, 1/2-z-1$	275.4(4)	150(6)
O-4′ $\overset{85(2)}{\longrightarrow}$ H-4O′$^{207(1)}$O-5	intramolecular	286.6(3)	157(3)

[a] A, Acceptor oxygen; D, Donor oxygen. [b] Standard deviations in parentheses.

2 should be the result of the preference of carbonyl oxygens to adopt positions synperiplanar to hydrogens in the γ-position, only. The dominant population of molecules of **2** locates O-61 1,3-parallel to H-61 (Fig. 2) with some freedom of O-61 to move in the direction of H-62.

The positioning of the nitromethyl group is as usually observed (see above)[8]. As the glycosidic bond is concerned, C-5′ is found almost *trans* to C-2 and almost *gauche* to O-5 (torsion angles $-152.9(2)°$ and $85.8(3)°$, respectively). This finding is much more in accordance with the predictions of the exo-anomeric effect[9], as are the respective observations for α-maltose[13] and β-maltose monohydrate[11], for which the related values of -125.5 and $116.1°$ and of -116.6 and $123.1°$ have been reported[13]. In β-maltose octaacetate[12], these angles are -154.8 and $84.0°$, which is another indication of the similarities of this structure with that of **2**.

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