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Structure of 1,2,3,4,6,7-Hexa-*O*-acetyl-L-*glycero*-D-mannopyranose

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Abstract. $C_{19}H_{26}O_{13}$, $M_r = 462{\cdot}40$, orthorhombic, $P2_12_12_1$, $a = 18{\cdot}287\ (6)$, $b = 15{\cdot}543\ (4)$, $c = 8{\cdot}160\ (2)$ Å, $V = 2319\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}324$ g cm^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 9{\cdot}9$ cm^{-1}, $F(000) = 976$, room temperature, $R = 0{\cdot}041$, $wR = 0{\cdot}047$ for 2041 observed reflections. The pyranosyl ring has an undistorted $^4C_1$ conformation; bond distances and valence angles are in the range for carbohydrates. In the side chain, a *gg* conformation was observed for O(6) and a *gt* conformation for C(7). According to NMR data these conformations are also preferred in solution.

Introduction. The inner core region of lipopolysaccharides from bacteria of salmonella and *Escherichia coli* contains two essential building units: 3-deoxy-D-*manno*-octulosonic acid (KDO) and L-*glycero*-D-*manno*-heptose (Anderson & Unger, 1983), both chain-extended sugars. The KDO is connected by an α(2→6)-glycosidic linkage to lipid *A* (Imoto *et al.*, 1983), followed by the L-*glycero*-D-*manno*-heptose in an α(1→5)-glycosidic linkage. The latter is also linked to the outer core structure and the O-specific side chains (Brade, Zähringer, Rietschel, Christian, Schulz & Unger, 1984).

Additional saccharide branching is found at KDO and also at the heptose. KDO does not crystallize, but an X-ray structure analysis of its methyl ester tetraacetate has been carried out (Kratky, Stix & Unger, 1981). We have established a new synthesis of L-*glycero*-D-*manno*-heptose (Paulsen, Schüller, Nashed, Heitmann & Redlich, 1985) allowing improved availability of this compound. The free heptose does not crystallize, but we have succeeded in producing a crystalline hexaacetate, which was used for an X-ray structure determination. Of special interest is, as with KDO, the conformation of the side chain, especially in comparison with KDO.

Experimental. Platelet-shaped crystal, 0·3 × 0·1 × 0·2 mm, Stoe four-circle diffractometer, θ–2θ scan at room temperature, Ni-filtered Cu $K\alpha$ radiation. Lattice parameters determined from 44 high-order reflections ($40 \leq \theta \leq 45°$). One octant (all $hkl \geq 0$) of independent reflections measured, $(\sin\theta/\lambda)_{\max} = 0{\cdot}583$ Å^{-1}, 2216 reflections, 175 were classified as unobserved with $I < 2\sigma(I)$. The intensity was monitored by three standard reflections (460, 542 and 343) every 80 reflections (intensity variations of 2·0, 0·7 and 1·0%, respectively). Data were corrected for Lorentz and polarization effects, absorption and extinction were neglected.

Structure determination by direct methods (*MULTAN*; Main, Lessinger, Woolfson, Germain & Declercq, 1977). Least-squares refinement, *XRAY76* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), anisotropic thermal parameters for C, O, isotropic for H. H-atom positions from difference map or calculated; $R = 0{\cdot}041$, $wR = 0{\cdot}047$. Quantity minimized $\sum w(|F_o| - |F_c|)^2$, with $w = xy$, $x = 1$ for $\sin\theta > 0{\cdot}6$, $x = (\sin\theta)/0{\cdot}6$ for $\sin\theta \leq 0{\cdot}6$, $y = 1$ if $|F_o| < 14{\cdot}5$ and $y = 14{\cdot}5/|F_o|$ otherwise. Parameters for w were chosen so as to make $w.\Delta F$ almost independent of $|F_o|$ and $\sin\theta$. Unobserved reflections were included only if $|F_c| > |F_o|$. Maximum and average Δ/σ were 0·3 and 0·06, respectively. Residual difference densities less than 0·14 e Å^{-3}.

Discussion. Final atomic parameters are given in Table 1.* Bond angles are given in Table 2. The atom-numbering scheme and bond lengths are given in Fig. 1, a *SCHAKAL* (Keller, 1980) representation of the molecular structure is shown in Fig. 2. The pyranosyl ring has the expected $^4C_1$ conformation with an almost ideal chair geometry as can be seen from the ring

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* Lists of observed and calculated structure factors, anisotropic thermal parameters, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43059 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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torsion angles (Table 3) and the Cremer–Pople puckering parameters (Cremer & Pople, 1975) $Q = 0{\cdot}581\,(4)$ Å, $\theta = 5{\cdot}3\,(4)^\circ$, $\varphi = 38\,(4)^\circ$. Endocyclic bond lengths and angles are in the expected range for carbohydrates and need no further discussion. This also holds for the six acetyl groups. The averaged bond lengths [C—O 1·438 (15), O—C 1·355 (17), C=O 1·190 (6), C—C 1·479 (4) Å] compare well with previously determined acetylated carbohydrate derivatives (Luger & Paulsen, 1976).

The substituent at C(2) is axial, all other substituents are equatorial proving the *β*-D-*manno* configuration.

Of special interest is the side-chain conformation. The steric situation at C(6) is as follows: O(6) is *gauche–gauche* (*gg*), and C(7) is *gauche–trans* (*gt*) with respect to O(5) and C(4). This same side-chain configuration is preferred in solution, as was derived from ^{1}H NMR spectra. The $J_{5,6}$ coupling shows a small value of 2·4 Hz, which is to be expected for a *gauche* position of the protons H(5) and H(6) in the mentioned

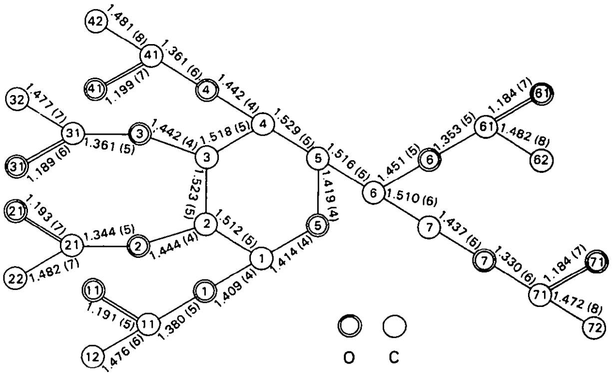

Fig. 1. Schematic drawing of the molecule showing numbering scheme used and bond lengths in Å (e.s.d.'s in parentheses).

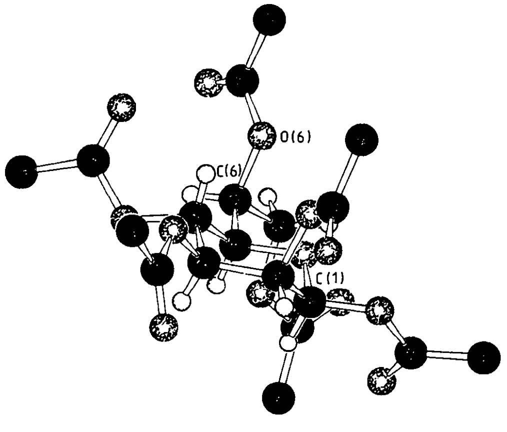

Fig. 2. A *SCHAKAL* view of the molecule. All methyl H atoms of the acetyl groups (omitted for clarity) were calculated theoretically, assuming that both staggered conformations with respect to the ether and the carbonyl O are occupied by 0·5 each.

Table 1. *Atomic parameters for* 1,2,3,4,6,7-*hexa-O-acetyl*-L-*glycero-β*-D-*mannopyranose* (U_{eq} *in* Å^2 × 100, *e.s.d.'s in parentheses*)

	x	y	z	U_{eq}*
C(1)	0·2829 (2)	0·1438 (2)	0·3827 (5)	4·8 (1)
O(1)	0·3387 (1)	0·1113 (1)	0·2808 (3)	5·24 (8)
C(11)	0·3184 (2)	0·0443 (2)	0·1795 (5)	5·8 (1)
O(11)	0·2586 (2)	0·0139 (2)	0·1814 (4)	7·9 (1)
C(12)	0·3802 (3)	0·0170 (3)	0·0756 (6)	7·3 (2)
C(2)	0·3169 (2)	0·1928 (2)	0·5235 (5)	4·8 (1)
O(2)	0·3607 (1)	0·2619 (1)	0·4575 (3)	5·24 (8)
C(21)	0·4297 (2)	0·2697 (3)	0·5119 (7)	6·9 (1)
O(21)	0·4556 (2)	0·2213 (3)	0·6093 (7)	12·5 (2)
C(22)	0·4660 (3)	0·3452 (3)	0·4367 (8)	8·9 (2)
C(3)	0·2555 (2)	0·2314 (2)	0·6261 (4)	4·7 (1)
O(3)	0·2852 (1)	0·2879 (2)	0·7495 (3)	5·44 (8)
C(31)	0·3137 (2)	0·2487 (3)	0·8844 (5)	6·4 (1)
O(31)	0·3099 (3)	0·1730 (2)	0·9035 (4)	9·2 (1)
C(32)	0·3493 (3)	0·3107 (4)	0·9962 (6)	8·5 (2)
C(4)	0·2039 (2)	0·2844 (2)	0·5209 (5)	4·8 (1)
O(4)	0·1406 (1)	0·3024 (2)	0·6203 (3)	6·10 (9)
C(41)	0·1144 (3)	0·3844 (3)	0·6229 (7)	7·4 (2)
O(41)	0·1401 (2)	0·4409 (2)	0·5411 (7)	10·6 (2)
C(42)	0·0489 (3)	0·3910 (4)	0·7290 (7)	9·9 (2)
C(5)	0·1790 (2)	0·2316 (2)	0·3729 (4)	4·7 (1)
O(5)	0·2404 (1)	0·2001 (1)	0·2854 (3)	4·83 (7)
C(6)	0·1326 (2)	0·2819 (2)	0·2522 (5)	5·2 (1)
O(6)	0·1762 (1)	0·3547 (2)	0·1995 (4)	5·94 (8)
C(61)	0·1398 (3)	0·4258 (3)	0·1492 (6)	7·0 (2)
O(61)	0·0755 (2)	0·4285 (2)	0·1339 (5)	8·9 (1)
C(62)	0·1917 (4)	0·4965 (3)	0·114 (1)	10·8 (2)
C(7)	0·1146 (3)	0·2299 (3)	0·1011 (6)	6·7 (1)
O(7)	0·0843 (2)	0·1499 (2)	0·1576 (4)	6·43 (9)
C(71)	0·0690 (3)	0·0915 (3)	0·0437 (7)	8·3 (2)
O(71)	0·0739 (4)	0·1067 (3)	−0·0981 (6)	14·7 (3)
C(72)	0·0473 (5)	0·0091 (4)	0·1182 (9)	12·6 (3)

* Calculated after Hamilton (1959).

Table 2. *Bond angles* (°) *for* 1,2,3,4,6,7-*hexa-O-acetyl*-L-*glycero-β*-D-*mannopyranose* (*e.s.d.'s in parentheses*)

O(1)—C(1)—C(2)	109·4 (3)	C(3)—C(4)—C(5)	110·0 (3)
O(1)—C(1)—O(5)	106·8 (3)	O(4)—C(4)—C(5)	108·0 (3)
C(2)—C(1)—O(5)	109·9 (3)	C(4)—O(4)—C(41)	118·3 (3)
C(1)—O(1)—C(11)	115·4 (3)	O(4)—C(41)—O(41)	122·6 (5)
O(1)—C(11)—O(11)	122·6 (4)	O(4)—C(41)—C(42)	111·0 (4)
O(1)—C(11)—C(12)	110·8 (3)	O(41)—C(41)—C(42)	126·3 (5)
O(11)—C(11)—C(12)	126·6 (4)	C(4)—C(5)—O(5)	110·2 (3)
C(1)—C(2)—O(2)	108·6 (3)	C(4)—C(5)—C(6)	113·8 (3)
C(1)—C(2)—C(3)	108·3 (3)	O(5)—C(5)—C(6)	107·1 (3)
O(2)—C(2)—C(3)	108·6 (3)	C(1)—O(5)—C(5)	111·5 (3)
C(2)—O(2)—C(21)	117·7 (3)	C(5)—C(6)—O(6)	106·7 (3)
O(2)—C(21)—O(21)	122·5 (4)	C(5)—C(6)—C(7)	112·2 (3)
O(2)—C(21)—C(22)	110·8 (4)	O(6)—C(6)—C(7)	107·2 (3)
O(21)—C(21)—C(22)	126·7 (4)	C(6)—O(6)—C(61)	117·1 (3)
C(2)—C(3)—O(3)	110·3 (3)	O(6)—C(61)—O(61)	123·4 (4)
C(2)—C(3)—C(4)	111·2 (3)	O(6)—C(61)—C(62)	110·4 (5)
O(3)—C(3)—C(4)	107·4 (3)	O(61)—C(61)—C(62)	126·1 (5)
C(3)—O(3)—C(31)	115·9 (3)	C(6)—C(7)—O(7)	106·5 (3)
O(3)—C(31)—O(31)	121·8 (4)	C(7)—O(7)—C(71)	116·6 (4)
O(3)—C(31)—C(32)	112·1 (4)	O(7)—C(71)—O(71)	122·0 (5)
O(31)—C(31)—C(32)	126·1 (4)	O(7)—C(71)—C(72)	111·3 (5)
C(3)—C(4)—O(4)	106·7 (3)	O(71)—C(71)—C(72)	126·7 (6)

Table 3. *Some dihedral angles* (°) *for* 1,2,3,4,6,7-*hexa-O-acetyl*-L-*glycero-β*-D-*mannopyranose* (*e.s.d.'s in parentheses*)

C(1)—C(2)—C(3)—C(4)	−53·6 (4)	H(2)—C(2)—O(2)—C(21)	−9 (2)
C(2)—C(3)—C(4)—C(5)	51·3 (4)	H(3)—C(3)—O(3)—C(31)	46 (3)
C(3)—C(4)—C(5)—O(5)	−54·4 (4)	H(4)—C(4)—O(4)—C(41)	13 (3)
C(4)—C(5)—O(5)—C(1)	62·5 (3)	O(6)—C(6)—C(5)—C(4)	58·0 (4)
O(5)—C(1)—C(2)—C(3)	59·9 (4)	O(6)—C(6)—C(5)—O(5)	−64·2 (3)
C(5)—O(5)—C(1)—C(2)	−66·0 (3)	C(7)—C(6)—C(5)—O(5)	52·9 (4)
H(1)—C(1)—O(1)—C(11)	39 (2)	C(7)—C(6)—C(5)—C(4)	175·0 (3)

conformation. It should be pointed out that for the triacetate of the KDO methyl ester not only in the crystal, but also in solution, another side-chain conformation exists. In this structure the atoms corresponding to the heptose O(6) and C(7) atoms exhibit *tg* and *gt* conformations, respectively. These deviations are comprehensible, since in KDO the C(5) substituent is axial, whereas the corresponding position of the heptose molecule shows an equatorial configuration.

However, the crystal structures of four derivatives of neuraminic acid are known (Biedl, 1971; O'Connell, 1973; Flippen, 1973; Wawra, 1974). All have the $^1C_4$ conformation, for which the stereochemical situation at the equatorially substituted C(6) atom is similar to the present structure: *gt* for the C atom and *gg* for the O atom of the side chain in question.

In the crystal structure of the title compound no close contacts of interest were observed.

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Structure of 2,2-Bis(methylthio)-1,1-ethylenedicarbonitrile

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Dedicated to Professor Dr K. Brodersen on the occasion of his 60*th birthday*

Abstract. $C_6H_6N_2S_2$, $M_r = 170{\cdot}3$, monoclinic, $P2_1/c$, $a = 4{\cdot}112$ (1), $b = 13{\cdot}406$ (1), $c = 15{\cdot}433$ (2) Å, $\beta = 111{\cdot}47$ (1)°, $V = 791{\cdot}7$ Å^3, $Z = 4$, $D_m = 1{\cdot}40$ (3), $D_x = 1{\cdot}43$ (1) Mg m^{-3}, $\lambda(\text{Ag } K\alpha) = 0{\cdot}5591$ Å, $\mu = 0{\cdot}255$ mm^{-1}, $F(000) = 352$, $T = 298$ K, final $R = 0{\cdot}047$ for 861 observed independent reflections. The molecules are arranged nearly parallel to the *bc* plane and form polar chains along the **b** direction. The molecule has a *syn–anti* conformation with respect to the $(MeS)_2C$ group as a consequence of reduced intramolecular steric interaction. The average S—C bond length is 1·762 Å. The central C—C is 1·368 Å.

Introduction. During our investigations on the existence and molecular geometry of the free acid $(HS)_2C{=}C(CN)_2$ we decided to study the more stable $(CH_3S)_2C{=}C(CN)_2$ (Hummel & Förner, 1986). The structure analysis of the title compound is also interesting from a more theoretical point of view. It exhibits unexpected redox behaviour in our cyclic voltammetric studies (Hummel & Procher, 1985) and shows a decreased charge density at C(1) compared with the dianionic species $(S_2C_4N_2)^{2-}$ (Henriksen & Eggert, 1978). It is expected that the geometry of the molecule can give some hint of the charge distribution and the repulsive electrostatic forces in the species.

Experimental. Stoichiometric amounts of $Na_2(S_2C_4N_2).3H_2O$ and CH_3I in methanol (Söderbäck, 1963). Crystal size 0·06 × 0·12 × 0·30 mm. D_m determined pycnometrically. Precession photographs. Monoclinic, Laue class $2/m$, systematic extinctions *h*0*l*,

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